DRAFT
REPORT ON FATE AND TRANSPORT OF MUNITIONS-RELATED MATERIALS

FOR THE
CAMP EDWARDS IMPACT AREA GROUNDWATER QUALITY STUDY

MASSACHUSETTS MILITARY RESERVATION
CAPE COD, MASSACHUSETTS

Prepared for

NATIONAL GUARD BUREAU
ARLINGTON, VIRGINIA

Prepared by

OGDEN ENVIRONMENTAL AND ENERGY SERVICES
239 Littleton Road, Suite 1B
Westford, Massachusetts 01886

File:\L:\mmr\ reports\archive\fate\dftrept

08/15/97

DISCLAIMER:

This document has been prepared pursuant to a government administrative order (US EPA Region 1 SDWA Docket No. 1-97-1019) and is subject to approval by the US Environmental Protection Agency. The opinions, findings, and conclusions expressed are those of the authors and not necessarily of the US Environmental Protection Agency.

TABLE OF CONTENTS

1. INTRODUCTION 1
  - 1.1 Background 2
  - 1.2 Constituents of Concern 3
    - 1.2.1 Organic COCs 3
    - 1.2.2 Inorganic COCs 4

2. EVALUATION OF CONSTITUENTS 8
  - 2.1 Organic Compounds 8
    - 2.1.1 Overview of Processes Affecting Fate and Transport 12
      - 2.1.1.1 Adsorption to Soils 12
      - 2.1.1.2 Solubility 12
      - 2.1.1.3 Volatilization 12
      - 2.1.1.4 Chemical Transformation 13
      - 2.1.1.5 Biological Degradation 13
    - 2.1.2 TNT 13
      - 2.1.2.1 Transformation 14
      - 2.1.2.2 Sorption 15
      - 2.1.2.3 Soil Binding 15
      - 2.1.2.4 Environmental Factors Affecting Fate and Transport 16
    - 2.1.3 RDX and HMX 17
      - 2.1.3.1 Transformation 17
      - 2.1.3.2 Sorption 18
      - 2.1.3.3 Environmental Factors Affecting Fate and Transport 19
    - 2.1.4 Other Explosive Materials 19
  - 2.2 Inorganics 20
    - 2.2.1 Processes Affecting Inorganic COCs 22
      - 2.2.1.1 Speciation 22
      - 2.2.1.2 Adsorption to Soils 22
      - 2.2.1.3 Precipitation in Soil Minerals 23
      - 2.2.1.4 Eh-pH Controls 23
    - 2.2.2 Antimony 23
    - 2.2.3 Arsenic 24
    - 2.2.4 Barium 25
    - 2.2.5 Boron 25
    - 2.2.6 Chromium 26
    - 2.2.7 Copper 26
    - 2.2.8 Lead 27
    - 2.2.9 Mercury 28
    - 2.2.10 Phosphorus 29
    - 2.2.11 Strontium 29
    - 2.2.12 Zinc 29

3. REVIEW OF OTHER SITE INVESTIGATIONS 31
  - 3.1 Erie Army Depot 32
  - 3.2 Fort Ord 32
  - 3.3 Fort Devens 32
  - 3.4 Valcartier Anti-Tank Range 33
  - 3.5 Louisiana Army Ammunition Plant 34

3.6 Cornhusker Army Ammunitions Plant ... 34
3.7 Summary of Observations ... 34
4. SITE-SPECIFIC FATE AND TRANSPORT MECHANISMS ... 36
4.1 Site Description ... 36
4.1.1 Physiography and Surface Waters ... 36
4.1.2 Hydrogeology ... 37
4.1.3 Potential Sources to Groundwater in the Impact Area and Training Range ... 39
4.1.3.1 Explosive Munitions ... 39
4.1.3.2 Small Arms Firing Ranges ... 40
4.1.3.3 General Activities ... 40
4.2 Previous Investigations ... 41
4.2.1 Point Source Investigations ... 41
4.2.2 Investigation of Diffuse Sources ... 44
4.2.3 Hydrogeologic Investigations ... 46
5. SUMMARY AND SITE CONCEPTUAL MODEL ... 47
5.1 Summary of the Literature Review ... 47
5.2 Site Conceptual Model ... 50
6. REFERENCES ... 53

LIST OF TABLES AND FIGURES

Figure 1-1: Chemical Structures ... 5
Table 2-1: Physical and Chemical Properties of Explosives ... 9
Table 2-2: Physical and Chemical Properties of Inorganics ... 21

1. INTRODUCTION

This report has been prepared to provide a general understanding of the fate and transport of munitions-related compounds in the soil and groundwater environment to assist in the interpretation of water quality information collected pursuant to ongoing investigations at the Massachusetts Military Reservation (MMR). This set of compounds includes explosive materials and their degradation products as well as inorganic materials associated with munitions (e.g., metals in casings, bullets, and primer materials). The scope of this effort consists of a literature review of the theoretical and applied research relative to the fate and transport of munitions-related compounds, a review of relevant studies at MMR, and a summary of case studies at other sites where munitions were used. It is intended that this information be relevant to assessments of the nature and extent of contamination at MMR. [Information on uptake, receptors, and environmental risk posed by munition-related compounds is not within the scope of this report.]

Contaminant fate and transport is affected by a number of factors, many of which vary significantly with site conditions. Most obvious among these factors are the physical, chemical, and biological properties of the materials themselves. This includes the water solubility, affinity for the soil solid phase, vapor pressure, and the susceptibility to biological and/or abiotic degradation. Many of these properties are strongly affected by site-specific biogeochemical conditions such as oxidation-reduction status, the nature of the solid phase, and concentration of chemical species that affect degradation. The other important class of site-specific conditions relates to the hydrogeological configuration of the site (e.g., groundwater velocity, depth to water table, rate of infiltration) which affects the residence time of consituents in the various portions of the site. Finally, contaminant fate and transport is affected by the means of release to the environment. A persistent source (e.g., an ongoing fuel release or sewage infiltration beds) would be expected to behave differently than a diffuse source present in surface soils. This report will provide perspective on all of these issues as they relate to the fate and transport of munitions-related materials at MMR.

This document is intended to provide a summary of available information on the fate of munitions-related materials. For example, literature observations of the persistence of explosives are summarized along with relevant analysis of contaminant hydrogeology performed under the Installation Restoration Program (IRP). This document presents preliminary conceptual models of the site-specific fate and transport of these materials. These preliminary models will be refined as data on the distribution of the munitions-related materials and hydrogeology of the Impact Area and its environs become available.

This report is organized to present an overview of the project, describe fundamental theoretical and applied research, summarize case studies, and present relevant MMR site data. Section 1.1 provides a project background summary. Section 2 presents an overview of fate and transport literature on munitions-related compounds. Section 3 summarizes some relevant case studies from other impact areas and facilities involved in manufacture and packaging of munitions. Section 4 presents site-specific information on fate and transport obtained from previous studies including those of IRP and the US Geological Survey (USGS). Section 5 provides a summary of findings and Section 6 presents references.

The munitions-related compound fate and transport literature review is covered in this document and provides complementary information to the overall program. This report is a companion to documents on the history of training range use (Odgen, 1997a) and the chemical composition of munitions (Ogden, 1997b).

1.1 Background

MMR is a 21,000 acre facility located in western Cape Cod. The facility consists of base administrative, housing, maintenance and operation facilities; ordnance training range and Impact Area; Veterans National Cemetary; and Cape Cod Air Force Station. Military use of MMR dates back to 1911. The training range and Impact Area consist of approximately 14,000 acres which have been used for Army National Guard, law enforcement and fire protection training. The training range and Impact Area consists of approximately 14,000 acres. The Impact Area contains targets at which artillery and mortars are fired during training activities. Numerous firing ranges, artillery and mortar positions, and training areas surround the Impact Area. For over 50 years, the training area and impact area have received ordnance discharged from small arms, guns, hand grenades, artillery, mortar, and ordnance demolition. The leaching of consituents associated with these materials has the potential to affect soils and groundwater. Because the groundwater underneath and downgradient of the training range is currently being considered for development as potable water supplies for four upper Cape towns, groundwater conditions in this area are the subject of an ongoing study.

Under the terms of an Administrative Order between the U.S. Environmental Protection Agency and the National Guard Bureau, Ogden, on behalf of the National Guard Bureau, is conducting an investigation to evaluate the effects of range training operations on the groundwater beneath the training range and Impact Area. The objectives of the investigation are to :

- Conduct a literature search to identify existing data and information and to determine the need for additional data to complete site characterization;
- Conduct an investigation of the training range and Impact Area to determine the effects of range training operations on groundwater quality.

As part of the Impact Area Groundwater Study, Ogden is currently performing the following activities:

- An archives search to ascertain the chemical composition of munitions as well as historical activities within the training range and Impact Area;
- Ordnance and Unexploded Ordnance (UXO) clearance of locations for subsurface investigation in the Impact Area and limited removal;
- Drilling and sampling of groundwater monitoring wells within the Impact Area and Training Ranges including upgradient and downgradient of the Impact Area;
- Evaluation of soil quality at various locations that are likely to exhibit impacts of historical activities; and
- An assessment of surface water, storm water, and sediment quality in the Impact Area and its environs.

1.2 Constituents of Concern

Munitions can be composed of metal parts, explosives, propellants, and pyrotechnics (e.g., flares). Munitions are designed so that the high energy organics are generally consumed during use. Munitions that explode upon impact generally consume the explosive compounds therein, leaving behind metal parts and other inert objects. Munitions that are employed and fail to function properly become UXO. Undetonated explosive compounds contained in UXO have the potential to leach to the environment. Munitions may include components such as bullets, cartridge containing propellents, high explosive chambers and primers. For the purposes of this report, Constituents of Concern (COCs) are defined as those constituents most commonly encountered during investigations of environmental fate and transport of munitions. These compounds are divided into organic compounds (i.e., explosives, propellants, pyrotechnics) such as TNT and inorganics (e.g., lead contained in bullets and primers).

This document focuses on those chemicals that are contained within munitions, especially high energy organic compounds that are unique to munitions. Some of the issues discussed in this document, particularly in Sections 4 and 5, apply to other compounds of environmental concern. For reviews of the fate and transport of other chemicals see Schwarzenbach et al. (1993) and Hemond and Fechner (1994).

1.2.1 Organic COCs

Many of the chemicals of potential concern at MMR at nitro-substituted molecules used in explosives and munitions. These fall into three catagories:

- Nitroaromatics such as 2,4,6-trinitrotoluene (TNT); 2,4-dinitrotoluene (2,4-DNT); N,2,4,6-tetranitro-N-methylaniline (Tetryl); picric acid, and styphnic acid;
- Nitramines such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraocine (HMX); and
- Nitrate esters such as pentaerythritol tetranitrate (PETN); nitroglycerin; and nitrocellulose.

These compounds are the high-energy organics identified in the evaluation of the chemical composition of munitions (Ogden, 1997b). The chemical structures of these compounds as well as several breakdown products are presented in Figure 1-1.

While munitions-related compounds have been of environmental interest for a number of years (see Kitchens et al., 1978), recent years have seen a great increase in their study. The literature on the environmental fate and mobility of explosive compounds is dominated by work on TNT, RDX, and HMX. These explosives are the most widely-used, have been found in the environment at other sites, and have been the focus of Department of Defense-funded investigation (Pennington, 1997). This document focuses on these three explosive materials as there is more extensive literature available. A number of degradation products of TNT (e.g., 4-amino-2,6-dinitrotoluene) are also considered. Finally, a variety of other organic compounds (e.g, PETN, tetryl, styphnate, picrate, nitrogylcerin) are also evaluated, although the literature on their fate and transport is less extensive.

The list of explosive materials considered is presented in Figure 1-1.

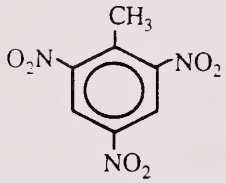
1.2.2 Inorganic COCs

The major component of small arms munitions is lead alloy with antimony added to enhance hardness. Other metal-jacketed munitions are copper-plated or covered with a thin layer of gilding metal, which may include copper and zinc. Arsenic is used in lead alloy for shotgun shot and may be present at ranges where shotguns were discharged. Based on the evaluation of the chemical composition of munitions (Ogden, 1997b), boron, chromium, phosphorus, barium, and strontium are also contained in munitions and have a potential for adverse environmental impact. Mercury is also included as it has been used in primer materials, although it was not identified as a munitions component in the munitions evaluated by Ogden (1997b).

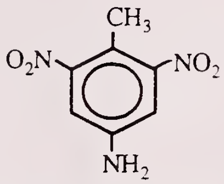
Based on this, antimony, arsenic, barium, boron, chromium, copper, lead, mercury, phosphorus, and strontium are, therefore, inorganic COCs for purposes of this report.

Figure 1-1:
Chemical Structures of Explosives

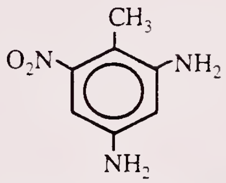
Nitroaromatics



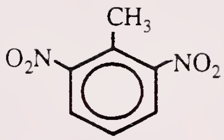
2,4,6-Trinitrotoluene
(TNT)



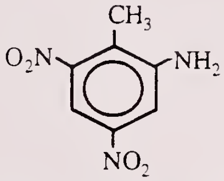
4-amino-2,6-Dinitrotoluene



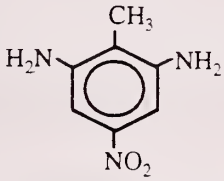
2,4-diamino-6-Nitrotoluene



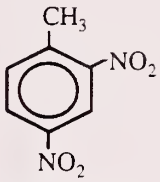
2,6-Dinitrotoluene
(2,6-DNT)



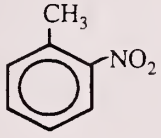
2-amino-4,6-Dinitrotoluene



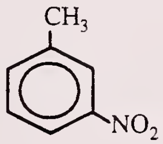
2,6-diamino-4-Nitrotoluene



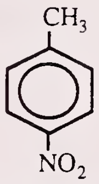
2,4-Dinitrotoluene
(2,4-DNT)



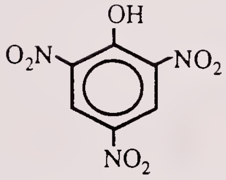
2-Nitrotoluene



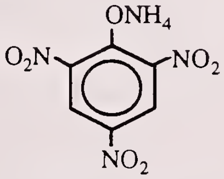
3-Nitrotoluene



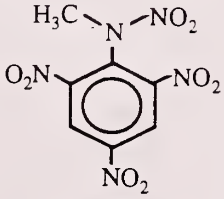
4-Nitrotoluene



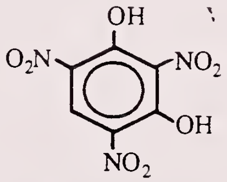
2,4,6-Trinitrophenol
(Picric Acid)



Ammonium Picrate



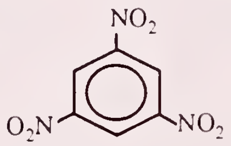
N-methyl-N,2,4,6-
Tetranitroaniline
(Tetryl)



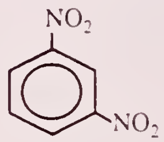
2,4,6-Trinitroresorcinol
(Styphnic Acid)

Figure 1-1 (Continued):
Chemical Structure of Explosives

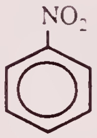
Nitroaromatics (cont'd)



1,3,5-Trinitrobenzene

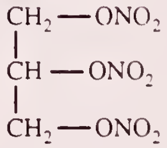


1,3-Dinitrobenzene



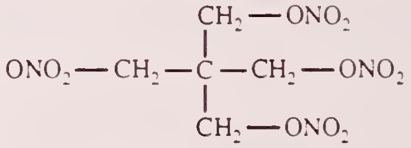
Nitrobenzene

Nitrate Esters



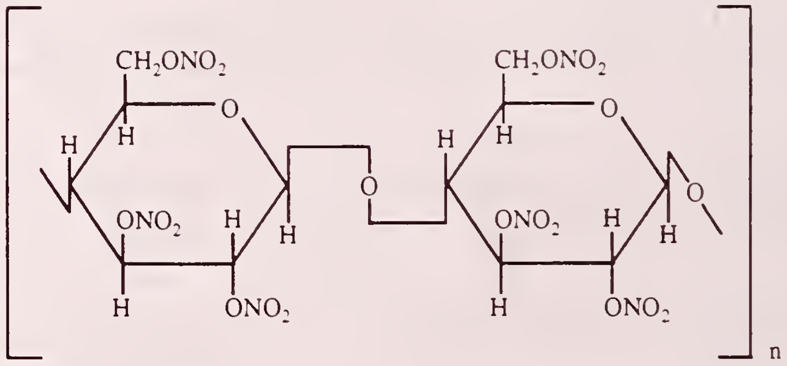
$$\begin{array}{l} CH_2 - ONO_2 \\ | \\ CH - ONO_2 \\ | \\ CH_2 - ONO_2 \end{array}$$

Nitroglycerin



$$\begin{array}{c} CH_2 - ONO_2 \\ | \\ ONO_2 - CH_2 - C - CH_2 - ONO_2 \\ | \\ CH_2 - ONO_2 \end{array}$$

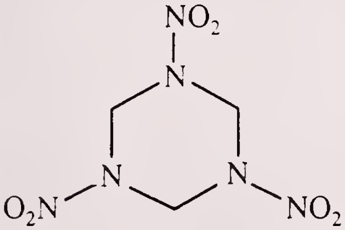
Pentaerythritol Tetranitrate
(PETN)



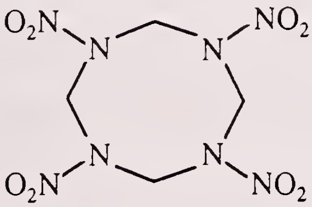
Nitrocellulose

Figure 1-1 (Continued):
Chemical Structure of Explosives

Nitramines



Hexahydro-1,3,5-trinitro-1,3,5-triazine
(RDX)



Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
(HMX)

2. EVALUATION OF CONSTITUENTS

This section provides a summary of fate and transport literature for munitions-related compounds. This section is organized to present information separately for organics and inorganics. A brief summary of important environmental processes affecting organic and inorganic materials is presented below. Following that general discussion are separate discussions of the various COCs.

2.1 Organic Compounds

The literature on the environmental fate and mobility of explosive compounds focuses on TNT, RDX, and HMX. These were widely-used high energy explosives and have been found in the environment at other sites. TNT and RDX/HMX are discussed separately, while the less well studied explosives are discussed together. An overall summary of fate and transport properties of the organic explosives and their breakdown products are provided as Table 2-1. The properties included in the table are:

- Molecular weight;
- Octanol-water partition coefficient (K_{ow} - l/kg), a measure of the chemical's hydrophobicity;
- Water solubility (mg/l);
- Vapor pressure (mm Hg), a measure of the chemical's propensity to move into the atmosphere;
- Henry's Law Constant (atm-m^3/mol), a description of the compound's tendency to move from water to air;
- Diffusion coefficients in air and water (cm^2/sec), quantities used to estimate rates of movement due to diffusion;
- Density of the pure compound (g/cm^3);
- Hydroxyl reaction rate constant (cm^3/mole-sec), a measure of the compound's ability to react with OH^- species present in water solution;
- pK_a, an expression of the compound's ability to lose protons (H^+) or act as an acid.

In addition to these properties, the CAS Number is listed along with the compound's empirical formula. The source of each datum is noted. The CAS number and empirical formula were obtained from the same source or were derived from the chemical name. If the datum is missing from the table, it could not be located.

Table 2-1:
Physical and Chemical Properties of Explosives

Compound	CAS Number	Empirical Formula	Source	Molecular Weight g	Source	Kow (l/kg)	Source	Water Solubility mg/l	Source
1,3,5-Trinitrobenzene	99-35-4	C6H3N3O6	3	213	1	1.5E+01	1	350	1
1,3-Dinitrobenzene	99-65-0	C6H4N2O4	3	168	1	3.1E+01	1	533	1
2,4,6-Trinitrotoluene	118-96-7	C7H5N3O6	3	227	1	4.0E+01	1	100	5
2,4-Diamino-6-nitrotoluene		C7H9N3O2		172		4.6E-01	4		
2,4-Dinitrotoluene	121-96-7	C7H6N2O4	3	182	1	1.0E+02	1	270	1
2,6-Diamino-4-nitrotoluene		C7H9N3O2		172		4.6E-01	4		
2,6-Dinitrotoluene	606-20-2	C7H6N2O4	3	182	1	1.1E+02	1	182	1
2-Amino-4,6-Dinitrotoluene	35572-78-2	C7H7N3O4		197	1	7.9E+01	1		
2-Nitrotoluene	88-72-2	C7H7NO2	3	137	3	2.0E+02	3	650	3
3-Nitrotoluene	99-08-1	C7H7NO2	3	137	3	2.8E+02	3	500	3
4-Amino-2,6-Dinitrotoluene		C7H7N3O4		197	1	7.9E+01	1		
4-Nitrotoluene	99-99-0	C7H7NO2	3	137	3	2.0E+02	3	650	3
Ammonium Picrate	131-74-8	C6H6N4O7	3	246	1	4.0E-02	3	10000	1
HMX (Cyclotetramethylenetrinitramine)	2691-41-0	C4H8N8O8	3	296	1	3.9E+00	1	2.6	7
Nitrobenzene	98-95-3	C6H5NO2	3	123	1	7.1E+01	1	2090	1
Nitrocellulose		--							
Nitroglycerin	55-63-0	C3H5N3O9	3	227	1	1.1E+02	1	1380	1
o-Chlorobenzylidenemalononitrile	2698-41-1	C10H5ClN2	3						
PETN (Pentaerythritol tetranitrate)	78-11-5	C5H8N4O12	3	316	1	4.0E+00	1	0.99	1
Picric Acid	88-89-1	C6H3N3O7	3	229	1	2.1E+01	3	13000	1
RDX (Cyclotrimethylenetrinitramine)	121-82-4	C3H6N6O6	3	222	1	7.2E+00	1	42	7
Styphnic Acid	82-71-3	C6H3N3O8	3	245	3	1.1E+01	3	5340	3
Tetranitrocarbazole									
Tetryl	479-45-8	C7H5N5O8	3	287	1	4.5E+01	1	80	1
	References:								
		1. IRP, 1994.							
		2. Merck, 1989.							
		3. Howard and Meylan, 1997.							
		4. Estimated According to Lyman et al., 1982.							
		5. Ro et al., 1996.							
		6. Burrow et al., 1989.							
		7. McGrath, 1996.							
		8. Haderlein et al., 1996.							

Table 2-1 (Continued):
Physical and Chemical Properties of Explosives

Compound	Vapor Pressure mm Hg	Source	Henry's Law Constant atm-m3/mol	Source	Diffusion Coeff. - Air cm2/sec	Source	Diffusion Coeff. - Water cm2/sec	Source
1,3,5-Trinitrobenzene	1.49E-07	1	1.60E-08	1	0.091	1	8.50E-06	1
1,3-Dinitrobenzene	6.75E-06	1	3.74E-07	1	0.105	1	9.53E-06	1
2,4,6-Trinitrotoluene	1.49E-06	1	4.57E-07	1	0.083	1	6.71E-06	6
2,4-Diamino-6-nitrotoluene								
2,4-Dinitrotoluene	1.10E-06	1	1.30E-07	1	0.098	1	8.95E-06	1
2,6-Diamino-4-nitrotoluene								
2,6-Dinitrotoluene	4.25E-06	1	7.74E-07	1	0.096	1	9.01E-06	1
2-Amino-4,6-Dinitrotoluene								
2-Nitrotoluene	0.188	3	2.35E-05	3	0.085	1		
3-Nitrotoluene	0.205	3	2.35E-05	3				
4-Amino-2,6-Dinitrotoluene								
4-Nitrotoluene	0.188	3	2.35E-05	3				
Ammonium Picrate	3.37E-11	3	2.94E-22	3	8.46E-02	1		
HMX (Cyclotetramethylenetrinitramine)	3.00E-09	1	3.50E-05	1	0.78	1		
Nitrobenzene	1.84E-03	1	1.90E-05	1	0.11	1	9.40E-06	1
Nitrocellulose				-				
Nitroglycerin	1.50E-06	1	4.30E-08	1	8.65E-02	1	8.10E-06	1
o-Chlorobenzylidenemalononitrile								
PETN (Pentaerythritol tetranitrate)	8.40E-04	1	3.16E-05	1	0.77	1		
Picric Acid	2.30E-07	3	3.80E-08	3	8.72E-02	1	8.51E-06	1
RDX (Cyclotrimethylenetrinitramine)	4.03E-09	1	1.90E-11	1	9.31E-02	1	8.87E-06	1
Styphnic Acid	2.57E-09	3	3.58E-11	3	8.14E-01	1		
Tetranitrocarbazole								
Tetryl	5.10E-09	1	2.69E-11	1	7.32E-02	1	6.94E-06	1

Table 2-1 (Continued): Physical and Chemical Properties of Explosives

Compound	Density g/cm3	Source	Hydroxyl Reaction Rate cm3/mole-sec	Source	pKa	Source
1,3,5-Trinitrobenzene	1.63	1	1.30E-15	3		
1,3-Dinitrobenzene	1.56	1	3.09E-14	3		
2,4,6-Trinitrotoluene	1.46	1	1.46E-13	3		
2,4-Diamino-6-nitrotoluene					3.13	8
2,4-Dinitrotoluene	1.52	1	2.25E-13	3		
2,6-Diamino-4-nitrotoluene					2.54	8
2,6-Dinitrotoluene	1.54	1	2.25E-13	3	1.8	3
2-Amino-4,6-Dinitrotoluene					0.36	8
2-Nitrotoluene			7.00E-13	3		
3-Nitrotoluene			9.50E-13	3		
4-Amino-2,6-Dinitrotoluene						
4-Nitrotoluene			7.72E-13	3		
Ammonium Picrate	1.72	1	1.13E-15	3		
HMX (Cyclotetramethylenetrinitramine)			3.30E-10	3		
Nitrobenzene	1.2	1	1.40E-13	3		
Nitrocellulose						
Nitroglycerin	1.6	1				
o-Chlorobenzylidenemalononitrile						
PETN (Pentaerythritol tetranitrate)			1.62E-12	3		
Picric Acid	1.76	1	3.69E-14	3	0.38	3
RDX (Cyclotrimethylenetrinitramine)	1.83	1				
Styphnic Acid			2.81E-13	3		
Tetranitrocarbazole						
Tetryl	1.57	1	1.27E-12	3		

2.1.1 Overview of Processes Affecting Fate and Transport

Processes that govern the persistence and mobility of organic compounds in soils and groundwater include adsorption, solubility in water, volatilization, photolysis, and chemical and biological transformations. Schwarzenbach et al. (1993) provide an extensive review of these processes. The following is a brief discussion of these phenomena.

2.1.1.1 Adsorption to Soils

Adsorption is the process by which a compound leaves water solution and associates with solid phase (i.e., suspended particles, soil particles, or aquifer solids). This association can act to reduce the water phase concentration and retard the movement of the compound relative to water infiltration through the unsaturated zone and groundwater. Affinity between compounds and immobile solids can take such forms as surface reactions or the partitioning of a hydrophobic organic molecule into a pool of organic material associated with the solids. These reactions can range in their reversiblity. The propensity for a compound to associate with solids is often observed to be subject to saturation, resulting in non-linear sorption behavior with increased chemical concentration in water (i.e., at high solution concentration, sorption becomes less efficient). The sorption behavior of the organic chemicals of concern to this study varies substantially between constituents due to intrinsic differences between the chemicals as well as site-specific conditions.

2.1.1.2 Solubility

Water solubility is a measure of the propensity of a compound to dissolve in water. In general, the higher the solubility the more mobile and less persistent a compound. Low solubility can act to limit the mobility of a compound by limiting its rate of movement into the mobile water phase. Reliable data on water solubility are generally available. The water solubility of the organic compounds of concern in this document range over several orders of magnitude.

2.1.1.3 Volatilization

Volatilization is the movement of the organic compound from a pure phase or water phase into vapor. The vapor may be contained within soils or be the larger atmosphere. Among the chemical properties that define a chemical's volatilization potential are its vapor pressure, its Henry's Law Constant (the ratio of the vapor pressure to water solubility), and the diffusion coefficients in water and air. In general, the organic compounds examined in this report are not likely to be subject to significant volatilization due to their low vapor pressures.

2.1.1.4 Chemical Transformation

Chemical transformation processes may include oxidation, reduction, and hydrolysis. An oxidation-reduction status of an environmental system refers to its ability to oxidize aqueous constituents. Abiotic oxidation-reduction reactions can be important to some of the organic explosive materials. The oxidation-reduction status of an aqueous system is affected by and helps determine which microorganisms are present. The oxidation-reduction status determines the dominance of various inorganic species which may affect the sorption status of some organics. Oxidation and/or reduction of organic compounds in groundwater may also occur by biotic means (see below).

A hydrolysis reaction involves the substitution of a water molecule for another atom (or group of atoms) present in an organic molecule. The compound is transformed into one with different properties. There are three forms of aqueous hydrolysis (acid, neutral, and base) which depend on the presence of different species in solution. Thus, different hydrolysis mechanisms can dominate at different pH levels. A hydrolysis reaction is essentially irreversible. Explosive organic compounds are generally resistant to hydrolysis except at high pH (i.e., pH greater than 9.0 - McGrath, 1995).

2.1.1.5 Biological Degradation

Biological degradation is a breakdown of the compound by microorganisms. This reaction is controlled by the type of microorganisms present in the system, their adaptation to the chemical of interest, the present of co-metabolites, and the oxidation-reduction status of the system. The rate of biodegradation is also dependent on the concentration of the chemical of interest (including its potential toxic effects to microbes) and the availability of nutrients and dissolved oxygen. The discussion presented below will focus on the potential for organic compounds to degrade under natural *in situ* conditions (i.e., in unamended soil or groundwater), although aA significant literature also exists on biologically-mediated treatment of explosives (e.g., wastewater treatement, phytoremediation, etc.- see Kaplan, 1995).

2.1.2 TNT

2,4,6-trinitrotoluene (TNT) is a single ring aromatic compound that is a crystalline solid at room temperature. The empirical formula for TNT is $C_7H_6N_3O_6$ with molecular weight of 227 g/mol. It's water solubility and vapor pressure are relatively low. Its K_{ow} indicates a moderate affinity for hydrophobic substances but sorption appears to be more complex than simple partitioning (see Section 2.1.2.2.2, below).

The major factors affecting the fate and transport of TNT in the subsurface are transformation, sorption, and irreversible soil binding (Townsend and Myers, 1996). TNT transformation generally occurs by sequential reduction of nitro groups to amino groups. Commonly observed reductive transformation products include 2-amino-4,6-dinitrotoluene (2A-DNT), 4-amino-2,6-dinitrotoluene (4A-DNT), 2,4-diamino-6-nitrotoluene (2,4-DANT), and 2,6-diamino-4-nitrotoluene (2,6-DANT) (see Figure 1-1 and Table 2-1). TNT transformation rates are enhanced significantly under anaerobic conditions. Depending on the oxidation-reduction potential (ORP as expressed as Eh), one or two of the nitro groups are reduced to amino groups. TNT is unstable at the Eh values of +500, +250, 0 -150 mV (Price et al., 1995). Hadelein and Schwarzenbach (1995) provide a review of the factors affecting reduction of nitroaromatic compounds including a summary of environmental redox potentials that lead to reduction of specific moieties.

2.1.2.1 Transformation

The microbial transformation of TNT has been studied extensively. TNT transformations in soils can occur both microbiologically and abiotically (Townsend and Meyers, 1996). Microbiogically-mediated degradation is typically faster than abiotic degradation, and is fastest under anaerobic (oxygen free) conditions (Townsend and Meyers, 1996). Complete mineralization of TNT has been documented through co-metabolism (TNT was not the only source of carbon for the microorganisms) under aerobic conditions (Gunnison et al, 1993). When sterilized and unsterilized soils were used, transformations were observed under both conditions (Pennington and Patrick 1990), suggesting the presence of a purely abiotic transformation component. Transformations were far more extensive in unsterilized soils than in sterilized soils. TNT transformations in water exposed to plants and sediments produce products similar to those produced with soils, particularly mono- and di-amino reduction products (Palazzo and Leggett, 1986, Best and Sprecher 1996; Hughes et al., 1997).

Trinitrobenzene, isomers of amino-DNT and 2,4DNT were also generally present at detectable levels in soils containing TNT collected from sites such as arsenals, depots and ammunition plants (Walsh, 1990, Walsh and Jenkins, 1992). TNB is a phototransformation product (Burlinson, 1980), the amino-DNTs are biotransformation products (Jerger, et al, 1976) and 2,4-DNT is a manufacturing by-product (US Army, 1984).

Both Bruns-Nagel et al. (1996) and Bradley et al. (1994) observed the microbially-mediated transformation of TNT in soils containing microbes. Both studies were performed under aerobic conditions and led to initial production of amino-substituted breakdown products that were susceptable to further degradation. Bradley et al. (1994) observed mineralization of TNT. Bruns-Nagel et al. (1996) observed a 90% decline in extractable nitroaromatics in soils in 19 days. Thorne and Leggett (1997) observed a decline in TNT concentration in aerobic compost systems and note that with time, portions of the nitroaromatics become strongly bound to solids.

Several literature reviews are available on explosives degradation. Both Kaplan (1996) and Walsh (1990) summarize apparent degradation pathways for TNT and related compounds. Walsh focuses on in situ processes while Kaplan (1996) includes degradation pathways under treatment strategies.

2.1.2.2 Sorption

Sorption is an important process affecting the mobility of TNT. Partition coefficients have been derived for a variety of surface soils, although many of these studies failed to account for transformations of TNT during the experiments (Townsend and Meyers, 1996, Xue et al., 1995a,b). Partition coefficients (sorption) are higher for clay and silt than sand. Although some investigators have found a correlation between organic carbon content and TNT sorption, the primary sorption mechanism is sorption on inorganic surfaces (Pennington and Patrick, 1990). Where oxidation-reduction (redox) conditions and soil properties do not promote transformation, sorption may be a more important factor than transformation affecting TNT fate and transport (Brandon and Myers 1997).

Weismahr et al. (1997) examined the mechanisms of association between clay materials and nitroaromatic compounds. These authors hypothesize a mechanism for this strong association. This includes the observation that the nature of the cations in the bulk solution can affect the degree of sorption. The formation of clay complexes is thought to affect the nitroaromatics reactivity with respect to reduction as well as the rate of subsurface transport.

Differences in binding of TNT and 2,6-DANT to humic acids are observed Li et al. (1997). TNT binding isotherms are best described by the Langmuir model while 2,6-DANT exhibits a linear isotherm. Xue et al. (1995a,b) also observe non-linear sorption of TNT.

It should be noted that the classical model of sorption being correlated with the compound's organic carbon-water partition coefficient (K_{oc}) and the soil's fraction organic carbon (f_{oc}), does not appear to apply well to TNT (Jenkins, 1997a). Despite this, soil organic matter appears to affect the ability of TNT to sorb irreversibly to soil solids (Hundel et al., 1997).

2.1.2.3 Soil Binding

TNT can be sorbed in a reversible manner (Haderlein et al., 1996, Pennington and Patrick 1990) and can also undergo reactions, which can be mistaken for sorption, that remove TNT from solution and bind TNT transformation products to soil in an unextractable manner (Pennington et al. 1995a, Brannon et al. 1992, Price et al. 1995). Hundel et al. (1997) observed that 40% of sorbed TNT became irreversibly associated with humic acids. This process occurred after short equilibrium times.

2.1.2.4 Environmental Factors Affecting Fate and Transport

In considering the fate and transport of TNT and its transformation products, not only is the type of soil or sediment important, but also the ionic strength and composition of the groundwater or surface water in which the soil or sediment resides. TNT and its degradation products may exhibit very different mobilities in subsurface environments where specific adsorption to clay minerals can be a dominant sorption process (Haderlein et al., 1996). Competitive sorption between TNT, its degradation products, and other explosives has been postulated as a process that can effect their sorption and transport (Loehr, 1989; Ainsworth et al., 1993). For clay minerals, the competition efficiency of explosives and their degradation products parallels their relative distribution coefficient values (Haderlein et al. 1996). Competition between sorbed explosives is negligible only in very dilute systems. After the linear range for sorption is exceeded on clays, explosives with a higher distribution coefficient will displace compounds with a lower distribution coefficient. These phenomena are manifested as a reduction in the sorbed portion of the compound at high solution concentrations.

The fate and transport of TNT in the subsurface also depend on the environmental and geochemical conditions and the nature of the sorbing material. Sediments containing plants removes TNT from water more rapidly than does sediment alone (Best and Sprecher, 1996). Explosives maybe relatively stable in surface soils because of the presence of solid product (i.e., crystalline solids) in the soils (Pennington et al. 1995b) and the reduction in biodegradation due to the toxicity of explosives to soil organisms (Bradley and Chapelle 1995). Bradley and Chapelle (1995) also observed that soil moisture and co-metabolites facilitated degradation as did the presence of a mosaic of anaerobic and aerobic microbes.

Solution phase concentrations of TNT (and RDX and HMX) in soils containing high concentrations of these components, including a high proportion as free product, were controlled by the aqueous solubility of the respective explosives (Pennington et al. 1995b). This phenomenon leads to the observation of heterogeneity in soil concentration at fine scale (inches and feet) in impact areas (Crockett et al., 1996, Jenkins et al., 1996). Solution phase concentrations in soils with lower concentrations of explosives were controlled by partitioning (Pennington et al. 1995b). Diffusion was found to limit the movement of TNT from soil to water (Qaisi et al., 1996a). Qaisi et al. (1996b) concluded that plant-augmented TNT reduction rates were controlled by TNT dissolution and diffusion rates in soils. Jenkins (1997b) has performed unpublished experiments indicating that TNT dissolution was slow but more rapid than that of RDX or HMX. Jenkins (1997b) believes that this has important implications for the persistence of these compounds in soil and may explain why TNT has been observed at lower concentrations in the environment than RDX and HMX, despite use in similar quantities.

Comfort et al. (1995) examined TNT fate and transport through laboratory soil columns. They concluded that sorption (including irreversible association) and transformation affected TNT concentrations eluting from columns. Irreversible sorption accounted for 40% of sorbed TNT in long-term studies. The authors conclude that sorption behavior should not be described using linear models.

Volatilization is not an important environmental process for TNT. TNT exposed to sunlight degrades via photolysis (McGrath, 1996). The mechanisms of photodegradation are examined by Schmelling et al. (1996). Light accelerated TNT degradation by Fenton's reagent (Li et al., 1997).

Summaries of environmental fate of TNT and related nitroaromatics, including the potential for mathematical description, are provided by Brannon and Myers (1997) and McGrath (1995). Degradation mechanisms of nitroaromatics are also presented in Higson (1992). Spain (1995) edits a volume on the degradation of nitroaromatic compounds. The first chapter of this volume provides a review of biotic and abiotic degradation processes. Subsequent chapters deal with degradation by different types of organisms and present both theory and application data.

2.1.3 RDX and HMX

Both Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX or cyclonite) and Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) are crystalline solids at room temperature. Both have low water solubility and vapor pressure. Their K_{ow} indicate a low affinity for hydrophobic substances. RDX and HMX are primarily affected by transformation and sorption processes.

2.1.3.1 Transformation

RDX and HMX are affected by transformation. McCormick et al. (1981) suggested that RDX and HMX degradation occurs only under anaerobic conditions and degradation products would be susceptible to aerobic mineralization. Ongoing studies with radiolabeled RDX by Price et al. (in preparation), however, have shown that mineralization of RDX to carbon dioxide occurs under both anaerobic and aerobic conditions, but at approximately an order of magnitude higher rate under anaerobic conditions. First-order RDX and HMX transformation rate constants have been report to range from 0 to 0.1 hr^{-1} for RDX and from 0 to 0.09 hr^{-1} for HMX (Townsend and Myers 1996). Although several investigators have noted degradation of RDX and HMX under aerobic conditions, it appears to be dominated by clay and silt soils where anaerobic degradation may occur in microanaerobic zones. Other investigators believe that aerobic biodegradation of RDX and HMX is negligible (Jenkins, 1997b). It is suspected that RDX and HMX degradation are microbiologically mediated processes. RDX degrades to methanol, formaldehyde, hydrazine, and other nitroso-reduction products.

In contrast to RDX, HMX does not appear to be affected by transformation. In soil column experiments, Green et al. (1985) detected no transformation productes of HMX in column leachates. This result is consistent with the report of McCormick et al. (1984b) in that the eight-membered ring of HMX is apparently less susceptible to biotransformation than the six-membered ring of RDX.

Both Kaplan (1996) and Walsh (1990) summarize apparent degradation pathways for RDX and HMX. Walsh focuses on in situ processes while Kaplan (1996) includes degradation pathways under treatment strategies.

2.1.3.2 Sorption

Sorption is an important process affecting the mobility of RDX and HMX. Partition coefficients have been derived for a variety of surface soils (Townsend and Meyers, 1996). The impact of organic carbon content on sorption is unknown, although partition coefficients (sorption) are higher for clay and silt than for sand, indicating that sorption to inorganic surfaces dominates. As noted above for TNT, the model of chemical sorption developed for hydrophobic compounds (i.e., partition coefficient = $K_{oc} * f_{oc}$) does not apply well to RDX and HMX (Jenkins, 1997). The sorption of RDX can be described well using linear equilibrium sorption isotherms (Leggett 1985; Ainsworth et al. 1993; Selim and Iskander 1994; Haderlein et al. 1996). Clay content of natural soils and sediments is important to the sorption of RDX (Leggett, 1985).

Reported linear equilibrium distribution coefficients for RDX range from less that 1 to 7.8 L/kg whereas, linear equilibrium distribution coefficients for HMX as high as 13 L/kg have been reported (Townsend and Myers 1996, Xue et al., 1995a,b). Similar distributions coefficients were observed in column studies by Townsend et al. (1996). Nonlinear or nonequilibrium HMX sorption (breakthrough curve tailing) has been observed (Myers et al. in preparation; Pennington et al. 1995b). No loss (i.e., degradation or irreversible sorption) or RDX and HMX was observed by these authors. These values suggest that RDX is likely to be relatively mobile in soils and groundwater. The available information on HMX sorption suggests that HMX is mobile, although not as mobile as RDX. In general, RDX and HMX are sorbed to a lesser extent than is TNT (Townsend and Myers 1996). In contrast to TNT, only small amounts of RDX become associated with soil organic matter (Price et al. in preparation). The RDX removal from water was much less affected by the presence of plants than was TNT (Best and Sprecher 1996). However, low oxygen concentrations in the water resulted in increased removal of RDX relative to high dissolved oxygen concentrations (Best and Sprecher 1996).

Volatilization is not an important environmental process for RDX or HMX. RDX and HMX exposed to sunlight degrade via photolysis (McGrath, 1996).

2.1.3.3 Environmental Factors Affecting Fate and Transport

RDX has been reported to be resistant to biodegradation under aerobic conditions. However, under anaerobic conditions with supplemental organic nutrients, RDX degrades substantially. Clay content of natural soils and sediments is important to the sorption of RDX. HMX is observed to be more resistant to degradation than RDX but also appears to have higher affinity for solids. Jenkins (1997b) has observed that RDX dissolves more slowly than TNT and that HMX dissolves more slowly still. This suggests that HMX is more persistent than RDX, both of which are more persistent than TNT, HMX is expected to be most persistent as a crystalline solid in surface soils.

2.1.4 Other Explosive Materials

As presented in Figure 1-1 and Table 2-1, there are a number of explosive materials used in munitions besides TNT, RDX, and HMX. These other materials are less common and have received less study. For these reasons, they have not been subjected to the types of laboratory analysis of degradation and sorption that TNT and RDX/HMX have undergone. Despite this, these compounds are in widely used in munitions and their fate and transport bears consideration.

Some generalities regarding the likely fate and transport of these materials is possible. This is particularly the case for those nitroaromatics (e.g., tetryl, picric acid) that can be evaluated relative to the behavior of TNT based on their known physical-chemical properties (see Table 2-1). As a generality, the nitroaromatics can be evaluated based on the different substituents present on the aromatic ring (Lyman et al., 1982). For example, the water solubilities of picric acid and styphnic acid are greatly enhanced by the presence of the acid group on the aromatic ring. Similar changes are apparent in the vapor pressure and the Henry's Law coefficient. Thus, the basic properties (e.g., relatively low water solubility, low vapor pressures, and moderate to low affinity for organic phase solids) of these compounds can be hypothesized from chemical structure.

It is more difficult to estimate the specific sorption and degradation behavior of these molecules as these processes are complex functions of chemical structure. It can be hypothesized that the nitroaromatics will behave in a similar fashion to TNT with respect to sorption (i.e., moderate affinity for soil solids). The precise behavior is more difficult to predict. The rates of biodegradation are even more difficult to predict although differences in rates of loss of TNT breakdown products have been observed (see Spain, 1995). Kaplan (1996) summarizes the literature on environmental degradation of nitroaromatics such as tetryl and picric acid.

The remaining class of explosive compounds, nitrate esters, are also relatively poorly studied with respect to environmental behavior. Examples of this class include nitroglycerin PETN, and nitrocellulose. Physical-chemical properties of nitroglycerin and PETN are available. The water solubility of these compounds can be used to infer that nitroglycerin would be relatively mobile while PETN relatively immobile Nitrocellulose is unique in that it is a large polymeric molecule that will not enter water solution. Thus, it would be expected to be relatively immobile. Kaplan (1996) discusses mechanisms of degradation of the nitrate esters, including nitrocellulose.

2.2 Inorganics

The literature on the environmental fate and mobility of inorganic compounds associated with munitions focuses on antimony, arsenic, barium, boron, chromium, copper, lead, mercury, phosphorus, strontium, and zinc. These inorganics associated with munitions-related compounds, have been found in the environment at other munitions sites, and were identified as contents of munitions (Ogden, 1997b).

The determination of the relative environmental fate of compounds can be evaluated based on their physical and chemical properties and potential interaction with the environment. The important physical and chemical properties of the inorganic COCs that affect their behavior in the environment are presented in Table 2-2. This table includes:

- The atomic mass of the inorganic compound;
- Observed distribution coefficient, an expression of relative concentration in soils and water at equilibrium; and
- Common environmental oxidation and reduction forms.

It should be noted that the distribution coefficients for metals are likely to vary extensively depending on site-specific conditions. This includes significant variation that might occur within small distances at a given site. In fact, it is common to observe non-linearities in the relationship between solid and water concentrations, violating the basic assumption of the distribution coefficient. Despite these issues, the distribution coefficients presented in Table 2-2 provide a relative affinity for the given metal and the solid phase.

A compound's vapor pressure describes the volatility of a pure chemical at equilibrium. Generally, compounds with vapor pressures less than 10^{-6} mm Hg will be only minimally found in soil vapor and the atmosphere (Howard, 1989). Most of the inorganics described here have negligible vapor pressures at common environmental temperatures. The exception to this is mercury, which is discussed in Section 2.2.9.

A general summary of the fate and transport processes of inorganic materials is described in the next section. The typical behavior of the inorganic COCs in soil and water, based on the physical and chemical properties presented in Table 2-2, as well as previous studies at MMR, is discussed in the following sections.

TABLE 2-2
PHYSICAL AND CHEMICAL PROPERTIES OF INORGANIC CONSTITUENTS OF CONCERN AT MMR

		Distribution Coefficient, K_d		
Constituent	**Atomic Weight (g/mol)**	**Observed Range (ml/g)**	**Mean Value (Log K_d)**	**Common Redox Forms**
Antimony	121.75	NA	NA	Sb(III), Sb(V)
Arsenic	74.92	1.0 - 18 (1)	-	As(III), As(V)
Barium	137.34	NA	NA	Ba(II)
Boron	10.81	NA	NA	B(II)
Chromium	51.996	1.2 - 150,000 (1)	-	Cr(III), Cr(VI)
Copper	63.55	1.4 - 333 (1)	3.1 (1)	Cu(II)
Lead	207.19	4.5 - 7,640 (1)	4.6 (1)	Pb(II)
Mercury	200.59	NA	NA	Hg(0), Hg(II), Methylated Forms
Phosphorous (red)	30.97	NA	NA	P(0), P(VI)
Strontium	87.62	0.15 - 3,300 (2)	3.6 (2)	Sr(II)
Zinc	65.38	0.1-8,000 (1)	2.8 (1)	Zn(II)

Sources:
1) Dragun, 1988. Note that the range of the two redox species of chromium and arssenic are combined.
2) Baes, et al., 1984.

2.2.1 Processes Affecting Inorganic COCs

The persistence of metals in soils and groundwater, in contrast to that of most organic constituents, is not affected by degradation processes. The mobility of metals in these environments, however, is determined by the physical and chemical characteristics of each metal and of the site where it is found. Processes affecting metal mobility include dissolution-precipitation of soil minerals, adsorption-desorption on soil mineral surfaces, oxidation-reduction within soil and water, and formation of complexes with organic and inorganic molecules.

Natural background levels of many metals (e.g., copper, arsenic) may be relatively high in soils. Elevated metals in groundwater may result from a combination of three sources: (1) direct release by human activities; (2) mobilization of naturally occurring metals with changes in the chemical environment resulting from human activities; or (3) natural processes and background conditions.

Some of the metals contained in munitions (e.g., boron, strontium) are present as metals that are used because of their propensity to oxidize rapidly. These are likely to be oxidized either prior to entering water solution or soon afterwards. The literature on the environmental fate of inorganics generally deals with metal ions in solution rather than the metallic form. For this reason, the discussion presented below is dominated by consideration of the ionic form of these various inorganics.

The following is a brief discussion of the potential reactions affecting inorganic geochemistry.

2.2.1.1 Speciation

While metal concentrations are usually expressed as elemental abundances, they often occur as one or more dissolved complex species in combination with other elements. Hydrolyzed, methylated, and chelated inorganic species are known. Occurrence of these species may affect the solubility and bioavailability of an inorganic compound relative to the free ion alone.

2.2.1.2 Adsorption to Soils

Due to kinetic constraints on precipitation-dissolution reactions in soils, the most significant control on metal solubility in groundwater typically is adsorption to the surfaces of soil minerals. Metal ion substitution for hydroxyls and other species on mineral surface sites can be rapid and reversible, leading to a close approximation of equilibrium partitioning between dissolved and adsorbed metal concentrations. There are a number of factors influencing this partitioning, including the nature of the metal, the nature of the available mineral surfaces, and competition between chemical species for particular mineral surface sites.

Over certain concentration ranges, this partitioning may be nearly linear with water phase concentration. With higher concentrations, the effectiveness of adsorption is generally observed to decrease as mineral surface sites are occupied and no longer available to adsorb dissolved metals. At high metals concentrations in a particular soil, virtually all surface sites will be filled, and the soil's absorption capacity will, therefore, be exhausted, leaving any additional metals in the mobile solution phase.

If partitioning between aquifer solids and water is occurring, it will affect the velocity of the compound relative to groundwater.

2.2.1.3 Precipitation in Soil Minerals

Precipitation and dissolution of metal-bearing soil minerals such as oxides, hydroxides, and sulfides may exert a strong control on the solubility of particular metals. Such reactions are particularly noted with changes in the oxidation-reduction or pH state of the soil environment. It is very likely, at some locations, that metals react with available solutes resulting in reduced solubility.

2.2.1.4 Eh-pH Controls

Oxidation-reduction (Eh) and acid-base (pH) characteristics of soils and groundwaters are primary controls on metals mobility. Not only may different valence states of a particular metal have vastly different geochemical behavior, but also changes in Eh-pH may change both the dominant dissolved metal species and the adsorption capacity of soil minerals. For example, changes in Eh potential may alter the balance between sulfide and sulfate, changing the potential for precipitation reactions involving these two species. Similarly, the availability of hydroxyl ion may determine the effectiveness of metal adsorption to particular mineral surface sites.

There is no general rule for the Eh-pH behavior of particular metals. Some metals are more mobile in oxidized environments while some are less mobile. Still others are not directly influenced by Eh but may respond to the Eh behavior of other soil/groundwater constituents.

The behavior of the inorganic COCs with respect to these phenomenon is described below.

2.2.2 Antimony

Antimony is a silvery or gray lustrous metal. It has a low thermal conductivity and is combustible. Antimony is used in bullet metal to increase the hardness of the alloy.

Antimony in the environment tends to strongly adsorb to colloidal material in soil, which can be transported in groundwater (Battelle, 1996). In an oxidizing environment with mildly acidic to alkaline pH, the stable form of antimony is an anionic species (SbO_3^-). An anion has little adsorbtive affinity to soil organic material or clays because cation exchange usually dominates adsorption to clay (Battelle 1996). Sb(V) may be subject to leaching, depending upon the soil's free iron and manganese oxide content, pH, and texture. While the leaching may increase at both low and high pH conditions, the increase at high pH conditions is generally more significant. The chemical form of the released antimony is also pH sensitive. Under reducing conditions, elemental Sb (Sb^0) predominates, under mildly oxidizing conditions, Sb_2O_3 (Sb(III)) is the dominant species, and under highly oxidizing conditions SbO_3^- (Sb(V)) is the most important form (Dragun, 1988).

Under aerobic conditions in surface water, dissolved antimony is present primarily in the +5 oxidation state. Under reducing conditions, trivalent species such as $Sb(OH)_3$, $Sb(OH)_4^-$, and $Sb2S_4^{4-}$ predominate (Battelle 1996). Antimony can be reduced and methylated by microorganisms in the reducing environments and become more mobile. The resulting trimethylstibine initially may be oxidized by atmospheric oxygen to a mixture of trimethylstibine oxide, $(CH_3)_3SbOH$, and trimethylstibinic acid, $(CH_3)_2SbO_3H$, and then to antimony oxides and insoluble polymers. The oxidized antimony oxides are more soluble than trimethylstibine.

Neither the USGS nor IRP has developed generalities regarding the groundwater behavior of antimony.

2.2.3 Arsenic

Arsenic is a silvery to black, brittle, crystalline and amorphous metalloid. It has no stable isotopes. Arsenic is insoluble in water, caustic and nonoxidizing acids.

Arsenic exists in small-arms range soils mainly in elemental form in the bullet metal or as species leached from the bullet, oxidized to As(V), and sorbed onto soil minerals. Arsenic compounds in soils and sediments can undergo a complex series of transformations, including oxidation-reduction reactions, ligand exchange, and biotransformation (Battelle 1996). These fate processes are most strongly influenced by factors such as oxidation-reduction conditions, pH, the presence of certain competing anions and complexing ions, clay and hydrous oxide contents, metal sulfide and sulfide ion concentrations, and salinity. Arsenic tends to be more mobile under high alkaline and saline conditions. In addition, the presence of other ions and organic compounds can increase the mobility of arsenic due to competitive sorption and the formation of organoarsenic complexes. Arsenic may be biotransformed through methylation to form highly volatile arsine and its methyl derivatives, thus being transferred from sediments back to the water column in aquatic systems (Battelle 1996). The predominant form of arsenic in groundwater is arsenite but it may also occur as arsenate, depending on the characteristics of the water and the surrounding geology (Battelle 1996).

At MMR, the fate and transport of arsenic in groundwater is strongly influenced by redox reactions, which can affect changes in speciation, and therefore chemical reactivity (Cherry et al., 1994, Davis et al., 1993). The two forms observed in the Ashumet Valley Plume are As(III) and As(V). Thermodynamic predictions based on redox conditions of the Ashumet Valley Plume suggest that As(III) would be stable in the anoxic zone whereas As(V) would be the stable species in the suboxic zone as well as uncontaminated groundwater. Laboratory studies have shown that As(III) sorbs more weakly than As(V) on iron and aluminum oxides at mildly acidic pH values (Leckie et al., 1984, Davis and Kent, 1990, and Xu et al., 1991). As(III) is generally assumed to be more mobile than As(V) and this is observed in groundwater at MMR. The expectation is that, in the absence of reducing conditions, the mobility of arsenic would be limited by sorption of As(V) onto aquifer solids.

2.2.4 Barium

Barium is a silver-white, slightly lustrous, somewhat malleable metal with seven stable isotopes. Barium is extremely reactive and reacts readily with water, ammonia, halogens, and most acids.

Barium occurs in nature primarily as barite ($BaSO_4$) and witherite ($BaCO_3$), both of which are highly insoluble salts. In a study of the behavior of barium in soil, Lagas et al. (1994) observed that 18 to 39% of barium that was added to soil was subject to leaching. Complexation of barium ions is comparable to those of calcium (Schnoor et al, 1987). Barium ions form surface complexes with sand and exchange with H^+ and Al^{3+} (Lagas et al., 1984). Knowledge of the physiochemical forms of barium and its interaction with various ligands and particles in the natural water is relatively scarce (Lagas et al., (1984).

2.2.5 Boron

Boron can exist as a black hard solid, monoclinic crystals, or as yellow or brown amorphous powder. It is highly reactive and is insoluble in water but is soluble in concentrated nitric and sulfuric acids. Boron has a high neutron adsorption capacity and is amphoteric.

Elemental boron is a strong reducing agent is likely to be oxidized by water to B(III). $B(OH)_3$ tends to remain in solution except under low pH conditions with low concentrations of anions. Borate's behavior has been studied in the Ashumet Valley Plume, where it is essentially unreactive (i.e., highly mobile) (LeBlanc. 1984, Thurman et al., 1986). Chemical conditions (i.e., higher pH and anion concentrations) in the Ashumet Valley Plume are less favorable for boron sorption than those in the surrounding pristine groundwater. Thus, boron may adsorb somewhat more efficiently in otherwise uncontaminated groundwater.

2.2.6 Chromium

Chromium is a hard, brittle, semi-gray metal with oxidation states ranging from Cr(-II) to Cr(VI). The common environmental forms of chromium are Cr(III) and Cr(VI). Cr(III) is generally substantially less soluble and mobile than Cr(VI) (Syracuse Research Corporation, 1993). The two forms of chromium are interconvertable depending on the redox status of the aquatic system.

The fate and transport of chromium in groundwater is strongly influenced by redox reactions, which can affect changes in speciation and, therefore, chemical reactivity (Cherry et al., 1984, Davis et al, 1993). The two dominant redox forms of chromium exhibit substantially different mobilities. Cr(VI) is generally present as a relatively mobile, oxyanion. Cr(III) absorbs strongly to soil minerals and/or precipitates as chrome hydroxides and is, therefore, relatively immobile in groundwater. Thus, chromium mobility is favored by oxidizing conditions.

The chemical conditions in the uncontaminated (i.e., oxidized) groundwater above the Ashumet Valley Plume favor the formation of Cr(VI) and relative chromium mobility. In the mildly reducing zone of the Ashumet Valley Plume, reduction of Cr(VI) to Cr(III) and immobilization of Cr(III) results in the greatly reduced transport rate of chromium.

2.2.7 Copper

Copper leached from bullets is retained on soils through processes such as adsorption, ion exchange, complexation, and precipitation. Copper can occur in the environment as a free metal (Cu^0) or as Cu^{+1} or Cu^{+2} minerals. In solution, copper may occur in either the Cu^{+1} or Cu^{+2} oxidation states; however, the natural environment favors the more oxidized form (USGS, 1989). The mobility of copper is dependent upon compound solubility, type of ligands present, total organic carbon content available to complex with the metal species, soil type, pH, redox-potential, cation exchange capacity, and salinity. Strong retention generally occurs on soils rich in organics, or on carbonate and clay minerals, hydrous iron oxides, and manganese oxides when the amount of organic matter is low. Adsorption is the principal process between pH 5 to 6 whereas above pH 6, precipitation predominates (Battelle,1996). Copper has the highest potential for leaching in sandy soils with low pH values.

In waters containing dissolved carbon dioxide species, a strong ion pair, $CuCo_3$ (aq), may be the dominant form in oxygenated waters; whereas in solutions above a neutral pH, the form $Cu(OH)_{3-}$ may dominate.

The fate and transport of copper is strongly influenced by sorption onto sediment grains in the Cape Cod aquifer in the vicinity of MMR. Redox reactions involving copper are unlikely. Due to the mildly acidic pH and low concentrations of dissolved salts throughout much of the aquifer, there are few solubility controls on copper concentration by precipitation. On the other hand, free copper ion and its aqueous species are known to sorb strongly onto a wide variety of minerals (Sposito, 1984, Davis and Kent, 1990, Dzombak and Morel, 1990). The extent of sorption of free copper ions increases sharply with increasing pH and may be influenced by other solution conditions (Davis and Kent, 1990). While organic ligands can increase the mobility of copper ions, other metals (e.g., iron) compete efficiently for those ligands in the Ashumet Valley Plume leading to the relative immobility of copper (Kent, 1997).

2.2.8 Lead

The dissolution and mobility of lead derived from lead bullets and shot are primarily influenced by pH, precipitating agents (e.g., carbonates, sulfates, phosphates, sulfides), and sorbents (e.g., iron and manganese oxides and hydroxides, organic carbon, clays). The natural mobility of lead is low due to the low solubility of lead hydroxy carbonates (USGS 1989). Lead also tends to be adsorbed onto inorganic and organic surfaces, coprecipitates with manganese oxide, and has low solubility products. The mobility of lead is also influenced by cation exchange capacity and salinity. Generally, neutral or slightly alkaline conditions decrease the mobility of lead and acidic conditions increase it.

Once oxidized, lead can be precipitated in a variety of forms including hydroxides, sulfates, sulfides, carbonates, and phosphates. Each of these precipitates are soluble and are controlled by the site-specific water chemistry to which they are exposed. The solubility of lead depends primarily on pH, redox conditions, and the concentrations of the components that determine solubility. Generally, lead is more soluble under acidic (low pH) conditions. Precipitates such as phosphates and sulfides can be used to control lead solubility.

The sorption of lead ions onto sediment grains in the Cape Cod aquifer in the vicinity of MMR has limited its mobility in the Ashumet Valley Plume (Kent, 1997). It is unlikely that lead ions would undergo redox reactions once they are dissolved in water. While controls of lead solubility by formation of precipitates is possible, at the mildly acidic pH and low ionic strength of the uncontaminated aquifer, these reactions are relatively unlikely. Lead ions and its aqueous species are known to sorb extensively onto a wide range of minerals (Sposito, 1984, Davis and Kent, 1990, and Dzombak and Morel, 1990). This high degree of sorption is likely to result in the relatively poor migration observed beneath firing range berms at MMR.

Several field studies have been conducted to model or assess the mobility of lead from shooting ranges and small arms sites. These studies suggest that lead from munitions products remains largely immobile under a variety of environmental conditions (EA, undated). A significant study related to lead immobility was conducted at MMR in 1996 by US Army Corp. of Engineers Waterways Experimentation Station (WES). Elevated lead concentrations at three small arms ranges typically extended through the top 3 feet of soil, but diminished to below the detection limits beyond 6 feet (WES, 1996). Similar conclusions were reached by Argonne National Lab (1993) in its study of metal contamination at a training range in Germany. Surface soils and berms at the firing range contain high concentrations of lead and other metals. In some cases, these soils would be characterized under the Toxicity Characteristics Leaching Procedure, a relatively rigorous extraction procedure. In addition, plants and surface runoff in the area contained elevated lead concentrations. Despite this, lead is restricted to surface soils, suggesting that groundwater impact is unlikely.

Other studies confirmed the immobility of lead from munitions in the environment. For example, an investigation of the Lincoln Gun Club on Lake Michigan concluded minimal partitioning of sediment samples high in levels of lead from 73 years of activity into the surrounding waters (Potts, et al. 1993, cited by EA, undated). A 1992 study assessed the mobility of lead at a small arms range in various surface water and wetland areas in New Jersey. The data indicated that lead preferentially sorbed to suspended particulates in the water and rarely transported far from the original shot-fall zone (where the bullet originally landed). The data also expressed a relation between dissolution of lead to the pH: at pH equal to 6.3 concentrations of total lead of 1,270 µg/L and dissolved lead of 83 µg/L; at pH ranging from 7.0 to 8.4, concentrations of total and dissolve lead below detection limit of 1 µg/L (EA, 1997). Other studies cited by EA (undated), such as Lund et al. (1991) and Manninen and Tanskanen (1993), concluded lead immobility in transport limited biological uptake.

2.2.9 Mercury

Mercury is a liquid at room temperature, is highly volatile for a metal, and can exist in nature in elemental form, or either the mercurous (Hg_2^{2+}) or mercuric (Hg^{2+}) oxidation state. Of these three inorganic forms, the mercuric form is the most toxic (FDER, 1988).

Speciation of mercury compounds in an aqueous solution is chemically complex and is difficult to predict. Depending on pH, alkalinity, redox potential, as well as other variables, a wide variety of chemical species may occur. Additionally, in the aqueous environment under naturally occurring pH and temperature, mercury may become methylated by biological or chemical processes, although chemical methylation appears limited in occurrences. Methylmercury is the most hazardous of the mercury species due to its high stability and lipid solubility. In addition, its ionic properties that lead to an increased ability to penetrate membranes in living organisms (FDER, 1988). It has been noted that although the methylation process can occur under aerobic and anaerobic conditions, methylation seems to favor anaerobic conditions. Mercury, therefore, is a highly chemically active species whose fate and transport is determined by factors characteristic of both metallic and organic contaminants.

2.2.10 Phosphorus

The form of phosphorus that is of concern to this investigation is its elemental form (e.g., white phosphorus, P_4). This form is highly toxic but has the potential to form nontoxic phosphates (PO_4^{3-}). Walsh et al. (1996) note that little is known regarding the environmental behavior of phosphorus. These authors observed that white phosphorus was persistent in aquatic sediments in the absence of oxygen, which suggests a low water solubility. Walsh et al. (1996) also observed that aeration of sediments by exposure to air was extremely effective at destroying white phosphorus. This suggests that, in aerated soils and groundwater, phosphorus should not be persistent.

Phosphate mobility in the Ashumet Valley Plume is generally limited by strong sorption of phosphate onto iron oxide surfaces (Kent, 1997). The exception to this is in the most reducing sections of the plume where iron oxides are lost to reduction.

2.2.11 Strontium

Strontium is a pale yellow, soft metal that is chemically similar to calcium. It has four stable isotopes. It is soluble in alcohol and acids and decomposes water on contact. Strontium metal is a strong reducing agent and would be rapidly oxidized by water to Sr(II). Ion exchange reactions are likely to occur with Sr(II) as it behaves in a similar fashion to Ca(II). The sorption ability of strontium has been observed to be quite variable but the strong sorption is possible.

Neither the USGS or IRP have developed generalities regarding the behavior of strontium in soil or groundwater.

2.2.12 Zinc

Zinc is seldom found as a free metal in nature, but it does occur as the sulfide, oxide, or carbonate. It is a shining white metal with bluish-gray luster. Zinc is soluble in acids and alkalis but is insoluble in water.

Zinc occurs in the environment in the +2 oxidation state and may exist as a soluble zinc chloride, a less soluble oxide, a hydroxide, or a carbonate. The dominant fate of zinc is partitioning onto soil or sediments through sorption to hydrous ion and manganese oxides, clay minerals, or organic material. The mobility of zinc within soil, surface water, and groundwater depends upon the compound solubility, soil type, pH, cation exchange capacity, and salinity. As pH increases, zinc hydrolyzes to form $Zn(OH)_2$, $Zn(OH)_3^-$, and $Zn(OH)_4^{2-}$. In the presence of sulfur and carbon dioxide, ZnS and $ZnCO_3$ solids also form. Precipitation of zinc compounds is important only in contaminated or otherwise reducing environments. Generally, at low pH values, zinc remains a free ion. Zinc tends to be more readily adsorbed at pH values greater than 7 (Agency for Toxic Substances and Disease Registry 1992).

The behavior of zinc in the subsurface is similar to that of copper and lead. Its mobility is likely to be controlled by sorption to aquifer and soil solids. Precipitation may play a role but given background chemistry of the aquifer this is less likely to be important. Changes in zinc mobility are correlated with solution pH such that the background waters (pH approximately 5.8) are likely to result in higher zinc mobility than the waters within the Ashumet Valley Plume. Within the Ashumet Valley Plume zinc is estimated to move at approximately 10% of the rate of groundwater (Kent, 1997).

3. REVIEW OF OTHER SITE INVESTIGATIONS

There have been several data and/or information reviews of engineering and scientific literature to identify the nature of explosives contamination at military installations. These reviews have focused on the technical literature that identifies the processes that affect explosives and/or surrogate compounds. This includes evaluation of the nature and extent of soil and groundwater contamination in order to appraise the importance of source configuration as well as potential attenuation mechanisms. While the search has focused on settings similar to MMR (i.e., impact areas over sandy aquifers), other sites (e.g., manufacturing facilities) were also considered. This section provides a summary of the available data.

The documentation of field observations of explosive compounds in the environment provide the composite effects of the multiple processes that affect the fate and transport of explosive compounds. Most of the efforts have been directed at remediation, a logical result of the rudimentary understanding of the processes affecting fate and transport of explosives. Soil and groundwater contamination from explosives have been documented at several military facilities. However, due to the varied mode of contamination, environmental setting, and operational practices, very few of the sites reviewed can be considered to be similar to the Impact Area at Camp Edwards.

For the purposes of this archives search and review, several other military facilities were selected for review. These included:

- The North Post 40 complex at Fort Grayling training facility in Michigan;
- The archives search reports for Fort Ord and the Erie Army Depot in California and Ohio, respectively;
- The Installation Assessment of Fort Dix and Picatinny Arsenal, both in New Jersey;
- The assessment of the Ethan Allen firing range in Vermont;
- The archives search report for the Jefferson Proving Ground in Indiana;
- The Fort Meade RI/FS and site inspection reports for the BRAC land parcel;
- The site inspection and RI/FS reports for Fort Devens in Massachusetts;
- A technical report on the “Nonpoint source assessment at small arms ranges”;
- The literature review and site reconnaissance report for ordnance contamination at Fort Hunter in California;
- An investigation of an anti-tank training range in Valcartier, Quebec; and
- A preliminary assessment report for ordnance contamination at the former Pantex Ordnance Plant in Texas.

The general geology and mode of introduction of the contaminants at most of these sites were different from that at Camp Edwards; and in some cases, the hydrogeology is very different. Firstly, the water table at most of these other sites are more shallow than MMR, and the sites are not located in recharge areas, and/or in the primary aquifers of the regions. Furthermore, the subsurface materials of most of these sites inhibit contaminant migration due to their silt and/or clay contents; thus making the comparisons of these sites to that of the Impact Area difficult.

However, a review of some of the observations at these sites can provide valuable insight into the improvement of process descriptors and/or remedial technologies for field application. The former Erie Army Depot in Ohio, Fort Ord training facility in California, the Fort Devens Training ground in Massachusetts, the Valcartier anti-tank training range in Quebec, the Louisiana Army Ammunition Plant, and the Cornhusker Army Ammunition Plant in Nebraska have been selected as representative facilities for review because explosive compounds have been detected in the environment; and these sites represent a wide range of environmental settings.

3.1 Erie Army Depot

The former Erie Army Depot was a munitions testing facility established in 1918 in Port Clinton, Ohio. Data from the 1960s indicated that explosives and other industrial contaminants had entered the subsurface. However, the clayey nature of the soils prevented migration, and restricted the contamination to pockets of highly contaminated soils that could be addressed by source removal (McMaster et al, 1982). There was no contamination of groundwater by explosives at this facility.

3.2 Fort Ord

Fort Ord was established in 1917 on the Monterey Peninsula in California, and has small arms and artillery ranges, and maneuver areas (ESE, 1987). The soils are sandy, and are deposited over sandstone. These sands form a domelike topography of highly permeable materials that slope outwards from the center of the installation, similar to the configuration of the Impact Area. On the western border of the facility, these sandy soils are prone to coastal erosion. In spite of the high permeability, and the fact that there is documented contamination of groundwater by industrial solvents, explosive contamination is restricted to surface soils and to depths of four feet or less. The reasons for this have been postulated to be a result of the arid conditions and resulting low rates of infiltration, the low solubility of explosive compounds and the adsorptive capacity of the soils (U.S. COE, 1993).

3.3 Fort Devens

Fort Devens is located about 35 miles northwest of Boston, and has a similar hydrogeologic setting as Camp Edwards. The bedrock and glacial till are covered with permeable sandy glacial outwash. The only significant difference between the hydrogeologic environments at Fort Devens and Camp Edwards is that the glacial outwash is much thinner at Fort Devens. There are three major areas at Fort Devens: the North Post containing an airfield and a sewage treatment plant; the Main Post, which contains administrative offices and infrastructure; and the South Post. The South Post was, and continues to be, used for training. There is a centrally located impact area, several ordnance disposal areas, and small arms ranges. Intensive investigations of both soils and ground water were performed at these areas (ABB, 1993 and Ecology and Environment, 1994). Low levels of explosive compounds were found in groundwater at the EOD range, the Zulu range, and the Hotel range. These were all areas used for the disposal of ordnance by open burning. At the EOD range, four of 19 downgradient wells had detectable concentrations of RDX with a peak concentration of 7.9 µg/l. One of 19 downgradient wells had detectable concentrations of TNT, HMX, or PETN. At the Hotel range, 12 of 14 downgradient wells had detectable concentrations of RDX with a peak concentration of 17.9 µg/l; no other explosive compounds were detected. The Zulu range was used for both ordnance disposal and hand grenade training. Ten of 18 downgradient wells had detectable concentrations of RDX with a peak concentration of 390 µg/l. Nine of the 18 downgradient wells had detectable concentrations of HMX with a peak concentration of 23 µg/l. Other explosive compounds and degradation products were detected in one or two of the downgradient wells.

Monitoring wells were also placed around the impact area at Fort Devens, which contains the three ranges discussed above and studied in detail. Explosive compounds were detected in three of 17 monitoring wells around the perimeter of the impact area. No RDX concentrations in these perimeter monitoring wells exceeded 1 µg/l. There were sporadic concentrations above the limit of detection of other explosives

Metals were also analyzed for in all monitoring wells at the above sites. While there were concentrations above relevant standards, analysis of both filtered and unfiltered samples indicated that the high metal concentrations were associated with suspended sediments in the water and the true dissolved metal concentrations were below standards. The risk assessment of the impact area and the three ordnance disposal areas concluded there was no risk to human health from the groundwater. Ecological risk was also concluded to be insignificant, although continued monitoring of wetlands and ponds was recommended (ABB, 1993 and Ecology and Environment, 1994).

3.4 Valcartier Anti-Tank Range

Anti-tank training was performed at Valcartier, Quebec using explosive charges containing HMX (70%) and TNT (30%). Small amounts of RDX were contained in the primary charge of the munition. The rate of failure in these munitions was thought to be high and the munitions were also observed to sheer open and spill their explosive charges around the impact area (Jenkins, 1997b). Evaluation of surface soil quality (Jenkins et al., 1997) indicated a high degree of heterogeneity with respect to explosives concentration. In addition, HMX was present in soil at approximately 100-times the concentration of TNT. This is consistent with TNT's higher dissolution rate as well as its susceptibility to aerobic degradation. Shallow groundwater at this gravelly site did contain significant concentrations of HMX (approximately 300 μg/l).

3.5 Louisiana Army Ammunition Plant

The Louisiana Army Ammunition Plant, which is near Shreveport, was established in 1942 as a munitions loading and packing facility. The near surface geology consists of heterogeneous fluvial deposits of sand, silty sands, silty shale and clays that are up to 150 feet thick. There are several sites on the installation where pink water (waste water containing explosive compounds, so called because it appears reddish) were disposed of in lagoons. The largest of these sites was Area P. Area P soils were remediated in 1989 by incineration. A groundwater plume of RDX and TNT exists at Area P to the present. Concentrations of RDX and TNT are both above 1000 μg/l. These plumes of RDX and TNT are moving more slower than the groundwater due to sorption of explosive compounds on silts and clays (McGrath, 1995; ETA, 1991; Koch, 1997). Extensive testing of groundwater across the rest of the site shows that there are no plumes of explosive compounds that are not related to disposal of pink water in lagoons. There are sporadic detections of RDX around the load lines (factories where artillery shells were loaded with high explosives) with peak concentrations less than 100 μg/l (IT, 1997).

3.6 Cornhusker Army Ammunitions Plant

War time operations at the Cornhusker Army Ammunitions Plant in Nebraska, a munitions production and packing facility, resulted in the introduction of explosives into the subsurface. The geology at this facility consists of a relatively homogeneous fluvial, sandy gravel with some small scale sporadic and laterally discontinuous sand and silt lenses. There is a large plume of RDX in groundwater at this site, with some TNT, that has traveled across the installation boundaries. The source of the plume has not been positively identified, but is believed to be due to multiple sources of the which the most important were sumps where pink water was collected (and infiltrated into the sandy aquifer). The relative spatial distribution between the different types of compounds at this site demonstrates the differences between the physiochemical properties of the contaminants and their effects on the fate and transport in the environment. Despite a greater production of TNT (vs RDX) over a longer period, the TNT plume is only very slightly longer and wider than the RDX plume; indicating that TNT travels slower, probably as a result of aerobic biotransformation, and/or stronger sorption to the aquifer sands (McGrath, 1995).

3.7 Summary of Observations

The key observations from the review of other site investigations where there was contamination of the environment by explosive compounds are:

- Surface soil concentrations are affected by the relative solubility and degradability of TNT, RDX, and HMX. Although all three compounds have relatively low water solubility, as a crystalline solid HMX dissolves more slowly than the other two, contributing to its persistence in soils.
- TNT is less mobile than RDX, even in highly permeable, sandy aquifers with very little organic carbon;
- Advective transport, which depends on aquifer permeability, is a controlling factor in the transport of explosive compounds in the environment.
- Subsurface sorption and reaction processes may severely retard the transport of explosive compounds especially in the presence of clay soils.
- The severity of groundwater contamination is related to the type of release. Disposal of pink water at sites with sand aquifers has resulted in groundwater plumes of explosive compounds. Thus, the Cornhusker and Louisiana Army Ammunition Plants both have significant, mappable plumes resulting from pink water disposal. Ordnance disposal areas evaluated at Fort Devens resulted in small plumes of explosive materials. Impact areas at training ranges at Fort Ord and Fort Devens both have sandy soils and sand aquifers, but do not exhibit significant ground water contamination with explosive compounds. In the case of Fort Ord, impacts may be reduced by the low rates of infiltrating precipitation.

The most comparable site to Camp Edwards is Fort Devens. The two locations have similar climate, geology, and use. While the data are equivocal, at Fort Devens, contamination of groundwater with explosives is most obviously associated with ordnance disposal, not with the firing of weapons. There was no contamination of groundwater by explosives that could be positively associated with the impact area (where high explosive mortar rounds were fired). It should be noted that artillery was not fired at Fort Devens because of the post's smaller size. Despite this, substantial differences in the behavior of soil-associated explosives is not expected. Also, munition-related metals have not been detected in groundwater at Fort Devens. At another site with gravel-sites, significant groundwater contamination of shallow groundwater by HMX has been observed. This suggests that diffuse sources of explosives, such as impact areas, can have adverse impacts on groundwater quality.

4. SITE-SPECIFIC FATE AND TRANSPORT MECHANISMS

This section presents site-specific information that will affect fate and transport of munitions related materials at MMR. A description of the site is provided, along with a summary of previous investigations, existing information regarding contaminant sources, and a discussion of considerations governing fate and transport. In most cases, this involves a brief summary of investigations that are ongoing by the USGS and IRP. These two entities are collecting data on contaminant behavior and hydrogeology that are relevant to the Impact Area investigation. For example, descriptions of the behavior of metals by USGS and IRP are likely to be useful to this investigation. In addition, useful contrasts can be made between the situations being investigated by IRP and many of those in the Impact Area. Most notably, IRP is evaluating sources that have resulted in extensive, sharply-defined plumes. While such plumes may occur within the Impact Area, it is more likely that the dominant potential source to groundwater is more diffuse.

4.1 Site Description

The training range and Impact Area is in the northern portion of MMR. Numerous firing ranges, artillery and mortar positions, and training areas surround the Impact Area in the center of the training range. The Impact Area contains targets at which artillery and mortars are fired during training activities. These targets have been at relatively consistent locations through time. It is expected that the highest density of ordnance impacts occurred near these targets. Areas more distant from the targets are likely to be impacted but at a much lower rate. Demolition activities and training also occurred at designated areas. In addition, ordnance was disposed of in at least one location (CS-19). Small arms firing ranges are located at various positions around the Impact Area. These ranges contain spent munitions: Finally, other, less intensive and less well defined activities (e.g., disposal of waste oil from vehicle maintenance) occurred in troop training areas.

4.1.1 Physiography and Surface Waters

The Cape Cod peninsula was formed during the retreat of the glaciers at the end of the Ice Age. It consists of two distinct types of terrain resulting from the recession of two separate lobes of ice sheets. The training range and Impact Area are located on a broad, undulating glacial outwash plain with considerably more relief than the area to the south. The elevation generally ranges from 100 to 250 feet with a maximum reported elevation of 306 feet above mean sea level MSL) (ETA, 1997). The training range and Impact Area is dotted with natural depressions called “kettle holes”. Only one of these kettle holes, Succonsette Pond, which is located on the southwestern corner of the impact area buffer zone, consistently contains water.

Due to the high permeability of the sands and gravel underlying the training range and Impact Area, there are no perennial streams, and very little to no surface runoff. This suggest that almost all precipitation in the training range and Impact Area ends up as groundwater recharge or evapotranspiration. The rapid infiltration of rainfall essentially eliminates surface water runoff and ponding, even in most kettle holes. Intermittent streams are only visible in a few drainage swales, and are only active during heavy rainfall. Succonsette Pond appears to be fed from groundwater flow-through and runoff waters during heavy rainfall events. It has no surface water outflow. Topography of the range shows swales leading out of the Impact Area; others terminate within the range.

4.1.2 Hydrogeology

MMR is located within the Coastal Plain physiographic province. The predominant physical features are moraines and outwash plains composed of poorly sorted, heterogeneous mixtures of sands, silts, gravel, and boulder mixed with well sorted and stratified sands, gravel and silt. These geomorphologic features are a result of depositional processes associated with the advance and retreat of ice sheets. The training range and Impact Area is located on the north-central portion of MMR, which underlain by a geologic unit known as the Mashpee outwash plain. The geology is comprised of stratified, unconsolidated sands and gravels underlain by crystalline bedrock. The surface elevations typically vary between 100 and 140 feet above MSL in the outwash plains to about 300 feet above MSL in the moraines. The crystalline bedrock is at an approximate elevation of 150 feet below MSL (USAEHA, 1986).

The surface and subsurface soils are characterized by a heterogeneous mixture of cobbles, gravel, sand and silt to highly stratified sands and gravel. Typical of these soils are fine loamy topsoil overlying thick sand deposits or silty materials over stratified sand and gravel. All these deposits sit on a bedrock that has been mapped as a granodiorite (USGS, 1976).

The hydrogeology of western Cape Cod is strongly affected by the glacially-deposited aquifer materials (Masterson et al., 1997). The surficial sediments of the Impact Area and the surrounding region are comprised of four distinct units:

- The Mashpee Pitted Plain. This deposit consists of relatively coarse grained materials and extends from the a point approximately 2 miles from the Cape Cod Canal south and east to Nantucket Sound. The unit was formed as a delta. The surficial (delta topset sedimentary facies) consist of sands and gravels. The deeper, delta foreset deposits are generally finer consisting of medium to fine sand with small amounts of silt. The lowest unit is glaciolacustrine in origin and consists of layered fine sand and silt. The estimated hydraulic conductivity of these units generally decline with the increased fine fraction and so with depth. The ratio of horizontal to vertical conductivity is estimated to also change with increase in finer material. Thus, the proximal topset bed is estimated to have an horizontal hydraulic conductivity of 350 ft/day and the ratio of horizontal to vertical conductivity is estimated to be 3:1 (Masterson et al., 1997). For the distal bottomset bed, Masterson et al. (1997) have estimated a horizontal conductivity of 30 ft/day and a ratio of horizontal to vertical of 100:1.

- The Buzzards Bay Moraine. This unit is located near the western margin of Cape Cod and runs approximately parallel to the western coast. The Buzzards Bay Moraine is approximately one to two miles wide (east to west) and has very complex lithologic characteristics. The moraine has been observed to have numerous discontinuous lenses of fine-grained materials. While the hydrogeologic characteristics of the moraine deposits are believed to be less suitable for water supply (i.e., estimated hydraulic conductivity of 10 to 150 ft/day and wide variation in hydraulic characteristics - Masterson et al., 1997), the hydrogeology of the moraine is generally less well understood than that of the Mashee Pitted Plan.
- The Sandwich Moraine. The Sandwich Moraine is very similar to the Buzzards Bay Moraine in hydrogeologic characteristics. Masterson et al. (1997) describe the two units together and apparently find few distinguishing characteristics. The Sandwich Moraine Runs approximately parallel to Cape Cod Bay and is approximately one to two miles in width (north to south).
- The Buzzards Bay Outwash Deposits. These surficial deposits lie to the west of the Buzzards Bay Moraine and are apparently similar in nature to the deltaic deposits of the Mashpee Pitted Plain (i.e., a productive unit that is increasingly fine grained with depth).

Masterson et al. (1997) believe that all of these surficial units are underlain by lake-bottom beds of silt and clay. This unit is generally believed to be directly above the bed rock with an approximate thickness of 10 to 80 feet. The hydraulic conductivity of this unit is estimated to be 10 ft/day and the ratio of horizontal to vertical conductivity is estimated to be 100:1.

While the precise boundaries to each of the hydrogeological units is uncertain and there may be some degree of overlap with depth, the Impact Area apparently lies largely on the Mashpee Pitted Plain surficial unit. The two moraines lie at the western and northern edge of the Impact Area. Thus, activities ancillary to the Impact Area (e.g., gun positions) lie on moraine deposits. Given the water table configuration depicted by Masterson et al. (1996 and 1997), groundwater flow from the Impact Area is likely to include flow through the moraine deposits.

The aquifer present in western Cape Cod is generally an unconfined one. The water table surface (Masterson et al., 1997) exhibits a high point (elevation of approximately 65 feet above sea level) that incorporates the southeast portion of the Impact Area and extends to the south and east. The water table slopes away from the high point in all directions at approximately equal gradients. Based on this water table, groundwater flow from the majority of the impact area will likely be to the north and west. At the eastern and southern portions of the impact area, there is a possibility that groundwater flow is to the east and south.

It should be noted that while the general direction of groundwater flow can be hypothesized based on the groundwater contours, the precise path a potential plume would follow is more difficult to estimate. In particular, as pointed out by Masterson et al. (1996), plumes observed in other portions of the MMR are relatively narrow and are deflected horizontally and vertically by changes in the hydraulic conductivity of the aquifer materials.

Groundwater production wells have been developed around the edges of the Impact Area at a distance of approximately two to three miles. These wells are not currently in production. As they are brought into production, they have the potential to affect the groundwater flow patterns beneath the Impact Area.

The unsaturated zone beneath the impact area is very extensive. Masterson et al. (1997) presents cross-sections that indicate an unsaturated thickness ranging from 100 feet to in excess of 200 feet in the vicinity of the impact area. Borings completed at CS-19 indicated a water table at approximately 115 feet below ground surface.

Given the nature of the surficial materials at the Impact Area, infiltration through the unsaturated zone is expected to be relatively efficient. The rate of aquifer recharge has been estimated at 21 inches per year. Given the importance of recharge in the Impact Area, there is an expectation that downward vertical gradients may exist there.

4.1.3 Potential Sources to Groundwater in the Impact Area and Training Range

There are three known potential types of sources to groundwater at the Impact Area and Training Range: (1) use and disposal of explosive munitions; (2) small arms firing ranges; and (3) less intensive or well defined activities related to site use such as suspected disposal of waste oil from vehicle maintenance. This section describes the likely configuration of these source materials in soil and contrasts them to the sources that have been characterized under the IRP activities.

4.1.3.1 Explosive Munitions

Materials derived from munitions were deposited through two broad classes of activities: practice firing into the Impact Area and activities associated with disposal of munitions, propellants, etc. Practice firing is likely to result in projectile materials being introduced into a relatively broad area (e.g., several hundred feet around a target) but the materials (e.g., munitions fragments and/or unexploded ordnance) are likely to be distributed in a very heterogeneous fashion within that area (Jenkins et al., 1996). Projectile materials are not expected to be found at great depth. Unexploded explosive materials tend to retain their crystalline structure in the environment and to leach dissolved organics at a low rate (Jenkins, 1997a). Metal fragments would be expected to behave in a similar fashion. Therefore, a reasonable description of the projectile remnants is that each fragment acts as a localized, relatively low-grade source of its component materials. Evaluation of the potential impact to groundwater quality should consider the integration of these individual sources over the area(s) affected.

Practice firing may also result in the introduction of propellant materials into soils in the vicinity of the gun position. Such materials are likely to result from deposition of particles in air suspension and, therefore, are likely to be found relatively uniformly distributed in surface soils around the gun positions.

Materials disposal is likely to have taken three different forms: simple disposal onto the soil surface, burning of materials (e.g., propellant bags), and "wash-out" of propellant using water followed by disposal of the water on the ground. The first two of these activities are likely to result in relatively localized, uniform distribution of materials in soils. Wash-out activities have the potential to introduce materials in suspension and/or in solution deep into the unsaturated zone due to the rapid movement of the wash water through the soils.

4.1.3.2 Small Arms Firing Ranges

Practice firing of small arms has resulted in the presence of spent munitions in localized areas in the training range. In most cases, the spent munitions are concentrated in berms that lie behind target areas. In some cases (e.g., the Gravity Anti-Tank Range), it is likely that spent munitions are spread over larger areas outside of obvious surface features.

In all of these cases, the spent munitions have the potential to weather and release their component metals to the environment. The conceptual model described for the metal fragments of explosive ordnance is applicable in this case. Each fragment can be considered to be a low grade source of metal to the soil environment. The rate of metal leaching from the fragment is uncertain and definition of the rate is most amenable to evaluation through site-specific data collection.

Metals weathered from spent munitions will interact with soils prior to transport to the water table. This interaction has a significant potential to slow the rate of transport to the water table. Again, it is difficult to predict the degree of attenuation by soils and the results of this investigation will serve to evaluate that phenomenon.

4.1.3.3 General Activities

The final potential sources include a range of activities such as vehicle maintenance, potential application of pesticides and defoliants, etc. To the extent that these activities are understood, they are likely to represent either rather small point sources (waste oil disposal) or non-point sources (application of pesticides and defoliants) to groundwater.

In contrast to most of the source configurations described above, the IRP generally has responsibility for persistent sources that have given rise to extensive groundwater plumes. For example, the Ashumet Valley Plume derives from wastewater disposed of in infiltration beds. The wastewater has had a profound effect on the contaminant hydrogeology of the aquifer not only by acting as a source of materials but by changing the geochemical environment within the plume. For example, metals' mobility is affected by geochemical changes within the plume. Other source areas (e.g., the land fill and fuel spills) also represent major source areas that result in substantial persistent plumes.

While such behavior is possible in the potential source areas in the Impact Area and training (especially in the ordnance disposal areas), it is more likely that most of these sources could give rise to a more subtle and diffuse groundwater impact. In short, many of the sources are better conceptualized as non-point sources that are distributed over relatively wide areas. This should be considered during the interpretation of data from the Impact Area and training range.

4.2 Previous Investigations

Over the past two decades, numerous studies and investigations have been conducted to assess the nature and extent of contamination at sites associated with former operations at MMR, and to model the hydrogeological characteristics of the region. In comparing and contrasting sources of contamination at training range and gunnery sites versus IRP sites, it is important to recognize that the distribution of explosive-related materials at the former is often widespread over a given area and therefore diffuse in nature. This contrasts with IRP sites where tanks, impoundments, landfills, and other structures containing liquids, solids and leachate provide a major source of contamination within a defined area. Summaries of the previous relevant studies are categorized below as studies focusing on either point source contamination or diffuse source contamination.

4.2.1 Point Source Investigations

This section discusses those locations that can be considered to be point sources of contamination. These represent ongoing sources to groundwater that have resulted in a discernible plume in groundwater.

In 1978, analysis of a drinking water well used to support the Town of Falmouth revealed elevated levels of detergents in the vicinity of the MMR wastewater treatment plant. Sampling by the U.S. Geological Survey (USGS) identified a contaminant plume extending from the MMR wastewater treatment plant to the Ashumet Valley area of Falmouth.

Continued environmental studies between 1982 and 1985 acknowledged 73 sites that had potential to adversely impact soil and groundwater (MMR, 1997). As a result, 21 sites were designated as Priority One study areas based on potential for human exposure and contaminant release, while the other sites were designated as Priority Two and Three study areas. Areas of Contamination (AOCs) were defined as those sites that exhibited soil and/or ground water impact and posed a threat to the environment and/or the public. Site investigations conducted in 1987 for the 21 Priority One AOCs revealed detectable levels of volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), polynuclear aromatic hydrocarbons (PAHs), other semi-volatile organic compounds (SVOCs), waste oils, and metals.

Groundwater sampling activities in 1985 and 1986 that detected elevated levels of VOCs in a base well and several private wells in the Ashumet Valley area of Falmouth. Impacted ground water presumably resulted from the historic use and disposal of solvents and waste oils on the base (MMR, 1997).

Over the last ten years, investigation of groundwater contamination has shown that a number of distinct plumes have been established emanating from different source areas. Evaluation of these plumes allows for a number of generalities regarding contaminant fate and transport at MMR:

- The aquifer is unconfined and unsaturated soils are highly permeable. These phenomenon result in the strong susceptibility of the aquifer to impact from releases to soil. Thus, fuel spills, landfill leachate, and wastewater infiltration galleries have resulted in significant contaminant loading to groundwater.
- Groundwater velocity is rapid and the flow direction is relatively constant with time. This has resulted in the establishment of extensive plumes from the various source areas. These plumes are often sharply defined suggesting that there is little variation in flow patterns with time.
- While groundwater flow is largely outward from the regional water table high, the plumes have been deformed both vertically and horizontally in response to changes in aquifer conductivity and vertical hydraulic gradients (Masterson et al., 1996).
- The glacial moraine present to the west of Camp Edwards has not had a significant attenuating effect on groundwater contamination. This might be expected if the moraine contained extensive areas of fine materials as both the hydraulic conductivity might be reduced and sorptive capacity of the materials increased. In general, contaminant plumes appear to have migrated efficiently through the moraine. It has been hypothesized that heterogeneities within the moraine may result in different levels of contamination, causing a plume to appear patchy or fragmented. This might result from exclusion of the plume from tight materials or better flushing of more coarse materials. This phenomenon has not been definitively established (Walter, 1997).
- As described above under the discussion of inorganic fate and transport, the geochemical environment of plumes can have a strong effect on the fate and transport of metals. In most cases, the mobility of metals is reduced relative to that of groundwater. A complex set of processes affect metals' mobility and the plumes often change the background geochemistry

to affect the metals' mobility. The plumes may either increase or decrease metals' mobility relative to the background condition and in some cases both phenomena can be observed within a given plume (Rea et al., 1996, Kent, 1997).

- Organic contaminants within the aquifer undergo attenuation mechanisms such as sorption and degradation but, depending on the contaminant, may migrate significant distances from the source areas and persist for long periods of time (Barber et al., 1988). The nature of aquifer materials have been found to have a significant effect on the degree of sorption of organic constituents with fine sands and silts leading to greater attenuation than more coarse materials (Barber, 1994).

In 1987, the U.S. Army Environmental Hygiene Agency (USAEHA) directed a surface soil investigation to determine the impact of previous burning activities of propellant bags at artillery and mortar positions. Two gun positions (GP-8 and GP-9) containing the remains of ash residual from these activities were designated as representative sites for Chemical Spill -18 (CS-18) under IRP. Due to the immobility of the contaminants and the noticeable decline in concentrations of contaminants with depth, the report concluded that impacted soil associated with the ash residual was not hazardous and not a source of contamination. However, the report suggested that further analysis was necessary to completely evaluate the effects of explosive constituents. Specifically, the report cited a lack of environmental criteria for the compounds as well as limitations due to analytical detection limits (USAEHA, 1987).

In 1992, ABB Environmental Services, Inc. (ABB) conducted a site investigation at the CS-19 location within the Impact Area. The site was reportedly used as an unlined pit for ordnance deposition. The results of the soil sampling activities indicated the presence of several organic and inorganic chemicals, including explosives, in surface soils. However, the report concluded that impact to groundwater from this site was unlikely (ABB, 1992). Nevertheless, groundwater samples were collected from four groundwater monitoring wells at CS-19 to evaluate groundwater impact. The results of the analyses indicated that explosive chemicals (e.g., RDX) had migrated to the groundwater table (USACHPPM, 1996b).

In 1997, AFCEE continued efforts to investigate groundwater contamination associated with the CS-19 spill. Jacobs Engineering Group (1997b) conducted a supplemental groundwater investigation to define the affected hydrogeological area, determine the contaminants of potential concern (COPCs), define the extent of the off-site plume migration, and investigate potential upgradient sources. The study concluded that site CS-19 was a contributor of RDX and HMX contamination; however, the plume had not migrated beyond the edge of the Impact Area (Jacobs, 1997b). Other potentially site-related materials were also detected. The following is a discussion of the distribution of explosives as it apparently illustrates the fate and transport of those materials.

The concentrations of RDX and HMX in groundwater at CS-19 range from below the detection limits to 14 μg/l and 7.6 μg/l, respectively. The extent of impacted groundwater is relatively limited in that the concentration of explosives decreases with movement away from the apparent source. RDX and HMX are detected only detected in wells screened at the water table and not at wells screened deeper in the aquifer. RDX and HMX have not been detected at wells approximately 2000 feet downgradient. The concentrations of RDX and HMX were lower than observed in the same wells in 1994. No other explosive organics were detected in groundwater.

HMX was detected in surface and near surface soils in the 1992 investigation. No other explosive materials were detected in soils. No explosives were detected in the soil samples from 5 to 20 feet below the ground surface collected in 1996.

These data appear to be consistent with the information presented in Section 2 regarding the fate and transport of explosives. While TNT was likely disposed of with RDX and HMX, neither it nor its breakdown products have persisted in soils or groundwater. RDX is no longer apparent in surface soils, consistent with its relatively high mobility. Once in water solution, both RDX and HMX are relatively mobile and persistent, consistent with their observation in groundwater.

It should be noted that the activity at CS-19 consisted of ordnance disposal which may have included wash-out of explosives and propellents with water. This suggests that CS-19 is likely to be a strong source to groundwater, in contrast to more diffuse impacts such as contamination of surface soils by ordnance fragments. It should also be noted that groundwater contamination by RDX (at 0.86 μg/l) is observed upgradient of CS-19. The source of this material is not clear and impacts from diffuse surface sources cannot be ruled out.

4.2.2 Investigation of Diffuse Sources

There have been some investigations in areas that can be considered to be more diffuse in nature and thus, more representative of some of the potential source areas in the Impact Area and training range. This section discusses those investigations as models for the fate and transport of materials derived from the Impact Area.

In 1994, an aerial photographic site analysis (ERI, 1994) was conducted using aerial photographs dating back to 1943 to identify sites within the training range and impact area suspected to be potential sources of past contamination. Stereoscopic magnification aided in the analysis of characteristics associated with different environmental conditions based on color, texture, tone, shape, size and patterns associations The study identified several sites as showing evidence of burning and destruction indicative of targeting during weapons testing (ERI, 1994). This review was used in the scoping of this study and representatives of these areas are earmarked for investigation of soils and groundwater.

U. S. Army Center for Health Promotion and Preventive Medicine (USACHPPM, 1996a) conducted a follow-up investigation on the environmental impact from propellant burning bags at two firing positions, GP-8 and GP-9 (designated as CS-18). This study encompassed a research of historic activities at the firing locations and investigation of soil and groundwater impact. The results of these sampling activities indicated that the surface soil at the site (within one foot below grade) was impacted with explosives and heavy metals. No substantial groundwater contamination was observed at the site. In addition, the report indicated that the surface soil contamination posed little threat to groundwater which is located at approximately 80 feet below ground surface. A preliminary risk evaluation (PRE) incorporating these results concluded that current or continued use of the sites posed no imminent danger to human health or expected threat of ecological risk.

Between September 1995 and September 1996, The U.S. Army Corp. of Engineers Waterways Experiment Station (WES) conducted a study to determine the potential for vertical migration of metals from impacted areas at the small arms ranges located at Camp Edwards. The investigation involved soil sampling at three small arms ranges within the MMR contained by berms, which were assumed to be point sources for metal migration. During the two rounds of soil sampling at the three ranges, medium to high lead concentrations (i.e., up to 800 mg/kg) were restricted to surficial samples at less than 48 inches below the ground surface. Consistent with these data, two scenarios employing a one-dimensional advection-dispersion equation and the Multimedia Environmental Pollutant Assessment System (MEPAS) model predicted that it would take 125 to 300 years for the observed lead to migrate to groundwater (WES, 1996).

In 1997, AFCEE collected samples at a subset of the existing monitoring wells to measure the concentrations of total and dissolved inorganic contaminants in the groundwater underlying MMR. These data established a metals database to expand risk assessments conducted for the Technical Review and Evaluation Team (TRET) during the spring of 1996 (Jacobs, 1997a). The study also developed a conceptual model of the fate and transport of inorganic constituents in order to support the risk assessment process. Among the conclusions of this study were:

- Suspension of aquifer solids within groundwater samples have the potential to greatly affect observed groundwater concentrations. Jacobs (1997a) concludes that these suspended solids are not mobile with groundwater flow due to their intermittent nature. Thus, samples containing high suspended solids bias the estimated concentration of inorganics within the aquifer.
- The Ashumet Valley, FS-12, LF-1, and PFSA plumes are associated with low dissolved oxygen concentrations (DO) and oxidation-reduction potential (ORP) due to the microbial degradation of organic materials within the plume. Observations of low DO and ORP are accompanied by elevated concentrations of carbonate species, iron, manganese, and, in one case, orthophosphate. Iron and manganese are believed to be derived from the dissolution of soil minerals in the presence of low ORP. When groundwater leaves these reduced regions,

5. SUMMARY AND SITE CONCEPTUAL MODEL

This section summarizes the literature review presented above and presents a conceptual model of likely site behavior. The literature review includes information on the general fate and transport properties of munitions-related materials as well as a brief summary of ongoing investigations at MMR. The conceptual model is a refinement of the one presented in the Action Plan (ETA, 1997). The conceptual model is included in the Response Matrix and other site reports and will be further refined as site data become available.

5.1 Summary of the Literature Review

The following is a brief summary of the findings of the literature review presented in Sections 2 through 4.

The literature on the fate and transport of explosives has been expanded greatly in recent years. This literature has focused on TNT, RDX, and HMX and includes investigations of the sorption, abiotic transformation, and biodegradation of these compounds. This work has attempted to develop an understanding of the processes affecting explosives fate and transport (McGrath, 1994) as well as potential soil and water treatment strategies (Kaplan, 1996).

Based on this work, it can be concluded TNT is susceptable to both biotic and abiotic degradation, including aerobic biodegradation. The specific rates of loss are driven by site-specific conditions, thus it is difficult to predict a rate of loss a priori. Breakdown products of TNT are seen in environmental samples and may contribute to human health or environmental risks. Complete mineralization of TNT is also observed. Sorption to soil and aquifer solids is an important process in that it has been observed to affect the rate of TNT movement. Sorption is apparently non-linear with TNT concentration and is due to a combination of phenomena, with partitioning to organic carbon being a minor component. The presence of clay minerals is correlated with TNT sorption. Irreversible sorption of TNT has been observed. The low rate of dissolution of crystalline TNT can lead to its persistence in soils particularly where ponded water is unlikely.

Both RDX and HMX are generally less sorptive (i.e., more mobile) than TNT. Crystalline solids of RDX and HMX dissolve more slowly than TNT leading to persistence in soils. Distribution coefficients have been derived for both compounds and experiments suggest that sorption is linear with concentration. Sorption of these two compounds is observed to be a complex function of soil properties and is thought to be correlated with soil cation exchange capacity. Both of these compounds are relatively mobile once they are in solution. Both compounds undergo degradation in the environment but the rate varies widely with site specific conditions. Aerobic biodegradation is not thought to occur.

None of these three compounds undergoes significant volatilization. All are susceptible to photodegradation. Each occurs as a poorly water soluble crystalline solid that can limit their leaching from soils.

TNT and the related compounds that have received study can serve as models for the fate and transport of other nitrotoluene compounds. However, little is known regarding the environmental fate of nitrate esters.

The metals contained in munitions are, to some extent, typical of inorganic contaminants at any site. This is especially the case for those metals that are dissolved in soil or groundwater solution. In this environment, they are affected by a variety of complex reactions that can act to limit their solubility and mobility. It is difficult to quantitatively describe these behaviors without site-specific data. Data on the subsurface migration of inorganics from other studies at MMR are discussed in Section 3 to provide perspective on the likely environmental behavior of metals.

When present as spent munitions or munitions fragments, metals are likely to be relatively poorly available to the environment. As with explosives fragments, metal availability is likely to be limited by the rate of weathering of the fragment. This is, of course, distinct from some of the plumes present at the southern end of MMR where metals were released to the environment in water solution. This slow release of metals from spent munitions is apparent in the relatively shallow measurable impact of lead leached from firing range berms.

Review of previous munitions site investigations indicates that impact areas and training ranges have received relatively little study. Groundwater impacts from explosives are most often observed at facilities where explosives were manufactured or packaged. In many cases, the impacts are directly attributable to discharge of water solutions of the explosives to the subsurface. In situations where such groundwater impacts occur, clays and silts are observed to significantly limit the mobility of explosives. In sandy aquifers, explosive's mobility can be relatively high.

Available investigation of impact areas suggest that significant groundwater impacts are not generally associated with soil contamination by munitions residuals. The exception to this is at an impact area with a shallow water table and gravelly soils. Even in the presence of sandy aquifer material, no groundwater impact of such activities was observed at a site in California. The relatively low rates from precipitation may contribute to that phenomenon. Groundwater contamination observed at Fort Devens is most obviously associated with munitions disposal activities rather than munitions fragments in soil.

The observed groundwater concentrations of RDX and HMX at MMR are most immediately associated with such disposal activities. The distribution of RDX and HMX at CS-19 at MMR appears to be consistent with their relatively high mobility and persistence of these compounds. The absence of TNT and its breakdown products suggest that they are more susceptible to degradation than RDX or HMX.

The groundwater plumes present at MMR are generally the result of strong, persistent, and localized sources of groundwater contamination generally associated with liquid discharges. This has resulted in well defined plumes. To the extent that the Impact Area represents a non-point source of contamination to groundwater, the configuration of potential groundwater contamination is likely to be different. There is a potential that the source of contamination is so weak that attenuation mechanisms in soil and groundwater prevent a discernible impact to groundwater quality. Alternatively, the impacts to groundwater might be more generalized such that no organized plume is definable.

Inorganic contaminants in groundwater have received significant study at MMR. The mobility of these compounds is affected by the background geochemistry as well as the geochemistry of the plumes. Regions are observed within the plumes where inorganics are more mobile than in the balance of the aquifer. Changes in oxidation-reduction status are of clear importance to some inorganics with many toxic metals apparently more mobile under reducing conditions. These observations have been used to develop conceptual models of inorganics fate and transport.

While the geochemical status of the aquifer beneath the Impact Area is likely to limit metals mobility, there is a potential that localized reducing areas occur due to natural conditions or other contamination. For this reason, it is difficult to draw broad conclusions about the likely behavior of inorganics in the aquifer.

Organic contaminants are observed to be attenuated within the plumes existing to the south. The attenuation is not significant enough to limit significant migration of certain organic compounds. The degree of attenuation is affected by the aquifer material type with finer materials being more effective at attenuation.

The hydrogeology of the Impact Area and training range is relatively well established. Groundwater flow is likely to be radially outward from a groundwater high located in the southeast quadrant of the Impact Area. Groundwater flow regimes are likely to be similar to those observed to the south: radial flow is affected by vertical hydraulic gradients and changes in hydraulic conductivity. The rate of groundwater flow is high. The coarse nature of soils at MMR leads to very efficient infiltration and negligible surface runoff. Data collected on the lithology, hydraulic head distribution, and contaminant distribution will be used to refine the conceptual and numerical models of groundwater flow.

5.2 Site Conceptual Model

The following conceptual model of the site is developed based on the available site-specific data and the general literature on the fate and transport of munitions-related materials. As is clear from the summary provided in Section 5.1, much of the environmental behavior of both munitions and inorganics depends on site-specific hydrogeology and geochemistry. For example, in certain circumstances TNT is observed to be essentially immobile, whereas in others extensive groundater plumes are observed. Because this is the case, this conceptual model should be considered as preliminary and subject to revision when field data from the Impact Area become available. The conceptual model is presented in order to facilitate data interpretation.

The following conceptual model will be organized along the potential migration pathway of munitions-derived materials. In order, the elements of the potential migration pathway are:

- Deposited materials subject to leaching in surface and shallow subsurface soils;
- Migration of materials through the unsaturated zone with infiltrating precipitation; and
- Migration of materials in groundwater.

Each of these potential steps will be defined to the extent possible based on the available data. If major uncertainties exist around a process, this will be highlighted.

The munitions-related materials in and around the Impact Area are most likely to be found in surface soils. This is consistent with the majority of site activities as well as previous characterizations of the site. The possible exception to this is where suspected wash-out activities may have resulted in rapid infiltration of materials into the unsaturated zone. Disposal of other liquids (such as waste oil during troop training maneuvers) may also result in the introduction of contaminants deep into the unsaturated zone.

Generally, fragmented munitions (both organics and metals) are best considered to be very localized, low grade sources that accumulate over some area. Major outstanding questions to be resolved in this investigation are the density of the fragments (i.e., soil concentration) as well as the lateral and vertical extent of the affected area. In certain locations such as around gun positions, soils may be more uniformly affected by propellant materials. Outstanding questions in these locations is the concentration of materials in the soil as well as the lateral extent of the materials.

Given the high rate of infiltration likely to occur in the Impact Area and its environs, careful evaluation of the vertical transport of munitions-related material should be made. Two factors have the potential to limit the vertical migration to the water table: the relatively poor leachability of munitions materials from fragments and potential for reaction in, and sorption to, the unsaturated zone solids. The highly permeable soils are likely to preclude ponding of water on soils, slowing the rate of explosives dissolution. Sorption to unsaturated zone solids is likely to limit migration given the depth of the unsaturated zone at the Impact Area and the propensity of both explosives and inorganics to associate with solids.

While the original munitions fragments are likely to leach poorly regardless of conditions likely to be encountered, it is difficult to estimate the mobility of the materials once they enter water solution. The rate of sorption and degradation for munitions-related materials has been shown to vary substantially with site-specific conditions. Therefore, the vertical extent of munitions-related materials observed at the site will be important in refining the conceptual model. For example, existing data on the concentration of lead in soils beneath small arms firing ranges suggest that elevated lead concentrations have migrated only a short distance into the unsaturated zone. Alternatively, at CS-19, groundwater quality impacts are apparent despite the general lack of explosives in surface soils. Thus, it will be important to consider the soil conditions, the nature of the chemical, and the means of introduction when evaluating migration through the unsaturated zone. TNT is much more likely to be lost to aerobic degradation in soils and groundwater than either RDX or HMX. The latter two compounds have been observed to degrade in aerobic systems but the site of degradation is thought to be in anaerobic microzones.

Existing studies of similar areas suggest that materials present as fragments in surface soils are relatively immobile. This conclusion is based on the general correlation of groundwater contamination with release of explosives in water solution, either during wash-out or during disposal during manufacture. It should be noted that the source of low concentrations of RDX in groundwater upgradient of CS-19 has not been explained and could be due to effects of the widespread materials in surface soils.

As materials leave the bottom of the unsaturated zone, they will enter the groundwater. Migration in groundwater will occur according to the distribution of hydraulic head and hydraulic conductivity within the aquifer. From the Impact Area, groundwater will ultimately flow toward one of the coasts. Interaction with downgradient fresh surface waters is possible. In the near field, there is a possibility that flow will have a downward component. As described by Masterson et al. (1996), the groundwater flow paths are affected by changes in lithology within the aquifer. For this reason, it is difficult to predict the exact path of any potential groundwater plume. Groundwater transport velocities are generally believed to be relatively fast due to the high hydraulic conductivities of the various units. Based on the behavior of plumes to the south, the moraines are not likely to impede groundwater flow, but due to heterogeneities within the moraines, potential plumes may be diverted or appear to fragment.

Within groundwater, munitions-related materials will be subject to sorption, degradation, and dispersion. The effectiveness of these processes at attenuating downgradient concentrations is not clear at this point in time. In the presence of oxidizing conditions, many of the more important metals (e.g., copper, lead, zinc) are likely to be substantially slowed relative to groundwater. Explosives are likely to sorb poorly to the sand and gravel portions of the Cape Cod aquifer. Sorption will likely be more efficient in those units that contain clay minerals and other materials with greater surface areas. The effectiveness of degradation of the explosives materials is uncertain although the relatively oxidizing conditions of the aquifer suggest that degradation will be relatively slow. Groundwater dispersion within the aquifer may also act to reduce groundwater concentrations but the effectiveness of this process is difficult to gauge at this time.

6. REFERENCES

ABB Environmental Services, Inc. (ABB). 1992. Site Assessment, Work Completion Report-Chemical Spill Site in Impact Area, Massachusetts Military Reservation, Cape Cod,. November.

ABB. 1993. Final Remedial Investigation Report. Data Item A0009. Fort Devens, MA.

Agency for Toxic Substances and Disease Registry. 1992. Toxicological Profile for Zinc. Draft Update.

Anisworth, C.C., Harvey, S.D., Szecsody, J.E., Simmons, M.A., Cullinan, V.I., Resch, C.T., and Mong, G.H. 1993. Relationship Between the Leachability Characteristics of Unique Energetic Compounds and Soil Properties, Final Report, Project Order No. 91PP1800, U.S. Army biomedical Research and Development Laboratory, Fort Detrick, Frederick. MD.

Argonne National Lab. 1993. Heavy-Metal Contamination on Training Ranges at the Grafenwohr Training Area, Germanyl. ANL/ESD/TM-59.

Army Corps of Engineers. 1993. Archives Search Report, Fort Ord, CA. St. Louis District. December, 1993.

Baes, C.F., Sharp, R.D., Sjoreen, A.L., and Shor, R.W. 1984. A Review and Analysis of Parameters for Assessing Transport of Environmentally Released Radionuclides through Agriculture. Oak Ridge National Lab.

Barber, L.B. 1994. Sorption of chlorobenzenes to Cape Cod aquifer solids. Env. Sci. and Tech. 28:890-897.

Barber, L.B., Thurman, E.M., Schroeder, M.P., and LeBlanc, D.R. 1988. Long-term fate of organic micropollutants in sewage-contaminated groundwater. Env. Sci. and Tech. 22:205-211.

Barlow P.M. and Hess, K.M. 1993. Simulated Hydrogeologic Responses of the Quashnet Rive Stream-Aquifer System to Proposed Ground-Water Withdrawals. U.S. Geological Survey Water-Resources Investigation Report 93-4064.

Battelle. 1996. Draft Guidance for Conducting Environmental Assessments of Outdoor Small-Arms Ranges. Prepared for Naval Facilities Engineering Service Center. Port Hueneme, CA.

Best, E.P.H., and Sprecher, S.L.. 1996. Phytoremediation of explosives-contaminated groundwater using constructed wetlands, phase 1 report: plant screening study-submerged plant species. Draft Letter Report for Army Environmental Center, U.S. Army Corps of Engineers Waterways Experiment Station, Vicksburg, MS.

Bradley, P.M., and Chapelle, F.H. 1995. Factors affecting microbial 2,4,6-trinitrotoluene mineralization in contaminated soil. Environmental Science and Technology 29:802-806.

Bradley, P.M., Chapelle, F.H., Landmeyer, J.E., and J.G. Schumacher. 1994. Microbial transformation of nitroaromatics in surface soils and aquatic materials. Applied and Env. Microbiology. 60:2170-2175.

Brannon, J.M. and Myers, T.E. 1997. Review of Fate and Transport Processes of Explosives. Technical Report # IRRP-97-2. USCOE Waterways Experiment Station.

Brannon, J.M., Adrian, D.D., Pennington, J.C., Myers, T.E., and Hayes, C.A. 1992. Slow release of PCB, TNT, and RDX from soils and Sediments. Technical Report EL-93-38, U.S. Army Waterways Experiment Station, Vicksburg, MS.

Bruns-Nagel, D., Breitung, J., von Low, E., Steinbach, K., Gorontzy, T., Kahl, M., Blotevogel, K-H., and Gensa, D. 1996. Microbial transformation of 2,4,6-trinitrotoluene in aerobic soil columns. Applied and Env. Microbiology. 62:2651-2656.

Burlinson, N.E. 1980. Fate of TNT in the Aquatic Environment: Photodegradation versus Biotransformation. Final Report. Naval Surface Weapons Center.

Burrows, P., Rosenblatt, H., Mitchell, W. R., and Parmer, D.L. 1989. Organic Explosives and Related Compounds: Environmental and Health Considerations. Technical Report 8901. U.S. Army Biomedical Research & Development Command. Fort Detrick. Frederick, MD.

Cherry, J.A., Gillham, R.W., and Barker, J.F. 1984. Contaminants in Groundwater: Chemical Processes in Groundwater Contamination. Washington: National Academy Press.

Collins, W. et al. 1981. Installation Assessment of Fort Ord, CA. Prepared for US Army Toxic and Hazardous Materials Agency.

Comfort, S.D., Shea, P.J., Hundal, L.S., Li, Z., Woodbury, B.L., Martin, J.L., Powers, W.L. 1995. TNT transport and fate in contaminated soil. J. Env. Quality. 24:1174-1182.

Crockett, A.B., Craig, H.D., Jenkins, T.F., and Sisk, W.F. 1996. Field Sampling and Selecting On-site Analytical Methods for Explosives in Soil. Federal Facilities Forum Issue USEPA/540/R-97/501.

Davis, J.A., and Kent, D.B. 1990. Surface complexation modeling in aqueous geochemistry. In Hochella, H.F. and White, A.F. eds. Mineral-Water Interface Geochemistry. Reviews in Mineralogy. 23:177-260.

Davis, J.A., Kent, D.B., Rea, B.A., Maest, A.S., and Garabedian, S.P. 1993. Influence of redox environment and aqueous speciation on metal transport in groundwater. Preliminary results of tracer injection studies. In Allen, H.E., Perdue, E.M, and Brown, D.S. eds. Metals in Groundwater. Chelsea, MI: Lewis Publishers.

Dragun, J. 1988. The Soil Chemistry of Hazardous Materials. Silver Spring, MD: Hazardous Materials Control Research Institute.

Dzombak, D. and Morel, F.M.M. 1990. Surface Complexation Modeling. New York: John Wiley.

EA Engineering, Science, and Technology. Date Unknown. Lead mobility at shooting ranges. Prepared for Sporting Arms and Ammunition Manufacturers Institute, Inc.

Ecology and Environment. 1994. Remedial Investigation Report for Functional Areas I and II, Fort Devens, MA.

Engineering Technologies Associates (ETA). 1991. Prepare Groundwater Model for Selected Sites at the Louisiana Army Ammunition Plant, Shreveport Lousiana, USATHAMA contract DAAA15-89-D-0009/0002.

ETA. 1997. Action Plan for the Camp Edwards Impact Area Groundwater Quality Investigation. Prepared for the National Guard Bureau.

ERI. 1994. Aerial Photographic Site Analysis, Massachusetts Military Reservation Impact area, Barnstable County, Massachusetts. March.

ESE. 1987. Update of the Initial Installation Assessment of Fort Ord and Subinstallations: Presedio at Monterey and Fort Hunter Liggett. Prepared for US Army Toxic and Hazardous Materials Agency.

Florida Department of Environmental Regulation. 1988. A guide to interpretation of metal concentrations in estuarine sediments.

Green, B., Kaplan, D.L., and Kaplan, A.M. 1985. Degradation of Pink Water Compounds in Soil - TNT, RDX, and HMX. US Army Natick Research and Development Center Report TR-85/046.

Gunnison, D., Pennington, J.C., Price, C.B., and Myrick, R. 1993. Screening Test and Isolation Procedure for TNT-Degrading Microorganisms. Technical Report IRRP-93-2, U.S. Army Corps of Engineers Waterways Experiment Station.

Guswa, J.H., and LeBlanc, D.R. (1985). Digital Flow Models of Ground-Water Flow in the Cape Cod Aquifer System, Massachusetts. U.S. Geological Survey Water-Supply Paper 2209.

Haderlein, S.B. and Schawarzenbach, R.P. 1995. Environmental processes influencing the rate of abiotic reduction of nitroaromatic compounds in the subsurface. In Spain, J.C. (ed.) Biodegradation of Nitroaromatic Compounds. New York: Plenum Press.

Haderlein, S.B., Weissmahr, K.W., and Schwarzenbach, R.P. 1996. Specific adsorption of nitroaromatic explosives and pesticides to clay minerals. Env. Sci. and Tech. 30:612-622.

Hemond, H.F. and Fechner, E.J. 1994. Chemical Fate and Transport in the Environment. New York: Academic Press.

Hess, K.M., Davis, J.D., Fuller, C.C., and Coston, J.A. 1996. Spatial variability of metal-ion adsorption and hydraulic conductivity in a sand and gravel aquifer Cape Cod, Massachusetts. In US Geological Survey Toxic Substance Hydrology Program - Proceedings of a Technical Meeting, Colorado Springs, CO. September 20-24, 1993. USGS Water Resources Investigations Report 94-4015.

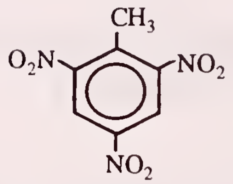
Higson, F.K. 1992. Microbial degradation of nitroaromatic compounds. In Advances in Applied Microbiology. Vol. 37. Neidleman, S.L. and Laskin, A.I. ed. pp. 1-19.

Howard, P.H. 1989. Handbook of Physical Properties of Organic Compounds. Volume 1: Priority Pollutants. Chelsea, MI: Lewis Publishers.

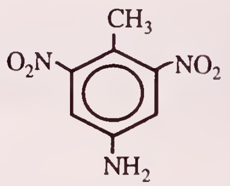
Howard, P.H. and Meylan, W.M. 1997. Handbook of Physical Properties of Organic Chemicals. Boca Raton: CRC Press.

Figure 1-1:
Chemical Structures of Explosives

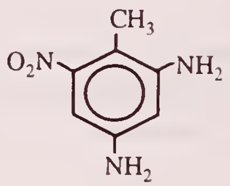
Nitroaromatics



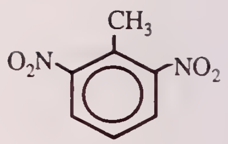
2,4,6-Trinitrotoluene
(TNT)



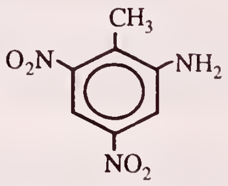
4-amino-2,6-Dinitrotoluene



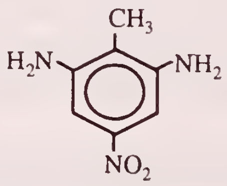
2,4-diamino-6-Nitrotoluene



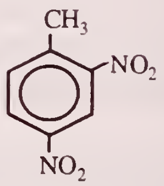
2,6-Dinitrotoluene
(2,6-DNT)



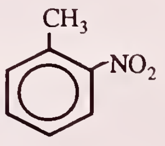
2-amino-4,6-Dinitrotoluene



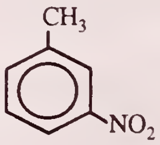
2,6-diamino-4-Nitrotoluene



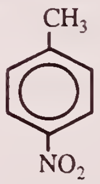
2,4-Dinitrotoluene
(2,4-DNT)



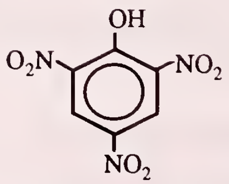
2-Nitrotoluene



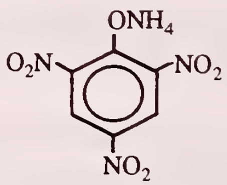
3-Nitrotoluene



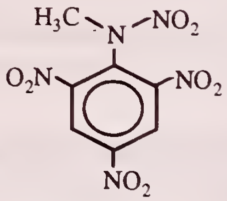
4-Nitrotoluene



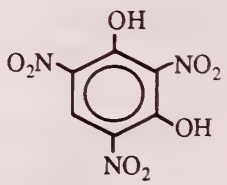
2,4,6-Trinitrophenol
(Picric Acid)



Ammonium Picrate



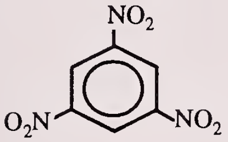
N-methyl-N,2,4,6-
Tetranitroaniline
(Tetryl)



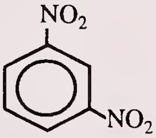
2,4,6-Trinitroresorcinol
(Styphnic Acid)

**Figure 1-1 (Continued):
Chemical Structure of Explosives**

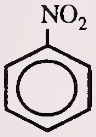
Nitroaromatics (cont'd)



1,3,5-Trinitrobenzene

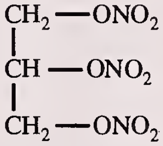


1,3-Dinitrobenzene



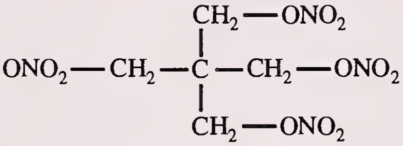
Nitrobenzene

Nitrate Esters



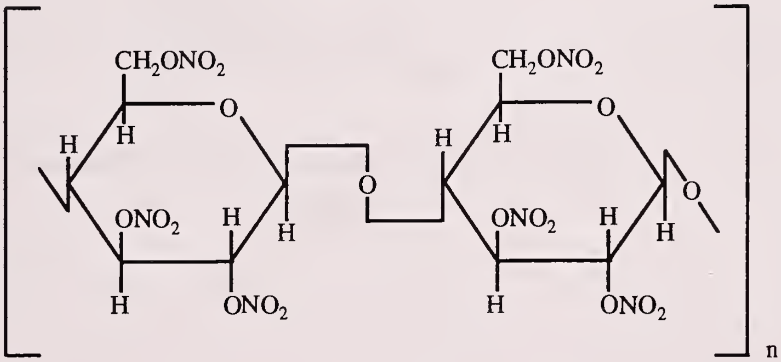
$$\begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array}$$

Nitroglycerin



$$\begin{array}{ccc} & CH_2-ONO_2 & \\ & | & \\ ONO_2-CH_2- & C & -CH_2-ONO_2 \\ & | & \\ & CH_2-ONO_2 & \end{array}$$

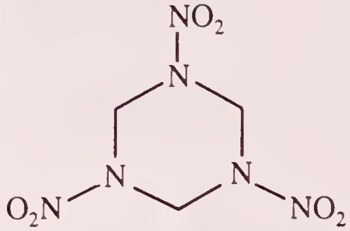
Pentaerythritol Tetranitrate
(PETN)



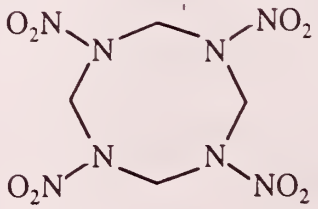
Nitrocellulose

Figure 1-1 (Continued):
Chemical Structure of Explosives

Nitramines



Hexahydro-1,3,5-trinitro-1,3,5-triazine
(RDX)



Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
(HMX)

Table 2-1:
Physical and Chemical Properties of Explosives

Compound	CAS Number	Empirical Formula	Source	Molecular Weight g	Source	Kow (l/kg)	Source	Water Solubility mg/l	Source
1,3,5-Trinitrobenzene	99-35-4	C6H3N3O6	3	213	1	1.5E+01	1	350	1
1,3-Dinitrobenzene	99-65-0	C6H4N2O4	3	168	1	3.1E+01	1	533	1
2,4,6-Trinitrotoluene	118-96-7	C7H5N3O6	3	227	1	4.0E+01	1	100	5
2,4-Diamino-6-nitrotoluene		C7H9N3O2		172		4.6E-01	4		
2,4-Dinitrotoluene	121-96-7	C7H6N2O4	3	182	1	1.0E+02	1	270	1
2,6-Diamino-4-nitrotoluene		C7H9N3O2		172		4.6E-01	4		
2,6-Dinitrotoluene	606-20-2	C7H6N2O4	3	182	1	1.1E+02	1	182	1
2-Amino-4,6-Dinitrotoluene	35572-78-2	C7H7N3O4		197	1	7.9E+01	1		
2-Nitrotoluene	88-72-2	C7H7NO2	3	137	3	2.0E+02	3	650	3
3-Nitrotoluene	99-08-1	C7H7NO2	3	137	3	2.8E+02	3	500	3
4-Amino-2,6-Dinitrotoluene		C7H7N3O4		197	1	7.9E+01	1		
4-Nitrotoluene	99-99-0	C7H7NO2	3	137	3	2.0E+02	3	650	3
Ammonium Picrate	131-74-8	C6H6N4O7	3	246	1	4.0E-02	3	10000	1
HMX (Cyclotetramethylenetrinitramine)	2691-41-0	C4H8N8O8	3	296	1	3.9E+00	1	2.6	7
Nitrobenzene	98-95-3	C6H5NO2	3	123	1	7.1E+01	1	2090	1
Nitrocellulose									
Nitroglycerin	55-63-0	C3H5N3O9	3	227	1	1.1E+02	1	1380	1
o-Chlorobenzylidenemalononitrile	2698-41-1	C10H5ClN2	3						
PETN (Pentaerythritol tetranitrate)	78-11-5	C5H8N4O12	3	316	1	4.0E+00	1	0.99	1
Picric Acid	88-89-1	C6H3N3O7	3	229	1	2.1E+01	3	13000	1
RDX (Cyclotrimethylenetrinitramine)	121-82-4	C3H6N6O6	3	222	1	7.2E+00	1	42	7
Styphnic Acid	82-71-3	C6H3N3O8	3	245	3	1.1E+01	3	5340	3
Tetranitrocarbazole									
Tetryl	479-45-8	C7H5N5O8	3	287	1	4.5E+01	1	80	1
	References:								
		1. IRP, 1994.							
		2. Merck, 1989.							
		3. Howard and Meylan, 1997.							
		4. Estimated According to Lyman et al., 1982.							
		5. Ro et al., 1996.							
		6. Burrow et al., 1989.							
		7. McGrath, 1996.							
		8. Haderlein et al., 1996.							

Table 2-1 (Continued):
Physical and Chemical Properties of Explosives

Compound	Vapor Pressure mm Hg	Source	Henry's Law Constant atm-m3/mol	Source	Diffusion Coeff. - Air cm2/sec	Source	Diffusion Coeff. - Water cm2/sec	Source
1,3,5-Trinitrobenzene	1.49E-07	1	1.60E-08	1	0.091	1	8.50E-06	1
1,3-Dinitrobenzene	6.75E-06	1	3.74E-07	1	0.105	1	9.53E-06	1
2,4,6-Trinitrotoluene	1.49E-06	1	4.57E-07	1	0.083	1	6.71E-06	6
2,4-Diamino-6-nitrotoluene								
2,4-Dinitrotoluene	1.10E-06	1	1.30E-07	1	0.098	1	8.95E-06	1
2,6-Diamino-4-nitrotoluene								
2,6-Dinitrotoluene	4.25E-06	1	7.74E-07	1	0.096	1	9.01E-06	1
2-Amino-4,6-Dinitrotoluene								
2-Nitrotoluene	0.188	3	2.35E-05	3	0.085	1		
3-Nitrotoluene	0.205	3	2.35E-05	3				
4-Amino-2,6-Dinitrotoluene								
4-Nitrotoluene	0.188	3	2.35E-05	3				
Ammonium Picrate	3.37E-11	3	2.94E-22	3	8.46E-02	1		
HMX (Cyclotetramethylenetrinitramine)	3.00E-09	1	3.50E-05	1	0.78	1		
Nitrobenzene	1.84E-03	1	1.90E-05	1	0.11	1	9.40E-06	1
Nitrocellulose								
Nitroglycerin	1.50E-06	1	4.30E-08	1	8.65E-02	1	8.10E-06	1
o-Chlorobenzylidenemalononitrile								
PETN (Pentaerythritol tetranitrate)	8.40E-04	1	3.16E-05	1	0.77	1		
Picric Acid	2.30E-07	3	3.80E-08	3	8.72E-02	1	8.51E-06	1
RDX (Cyclotrimethylenetrinitramine)	4.03E-09	1	1.90E-11	1	9.31E-02	1	8.87E-06	1
Styphnic Acid	2.57E-09	3	3.58E-11	3	8.14E-01	1		
Tetranitrocarbazole								
Tetryl	5.10E-09	1	2.69E-11	1	7.32E-02	1	6.94E-06	1

Table 2-1 (Continued):
Physical and Chemical Properties of Explosives

Compound	Density g/cm3	Source	Hydroxyl Reaction Rate cm3/mole-sec	Source	pKa	Source
1,3,5-Trinitrobenzene	1.63	1	1.30E-15	3		
1,3-Dinitrobenzene	1.56	1	3.09E-14	3		
2,4,6-Trinitrotoluene	1.46	1	1.46E-13	3		
2,4-Diamino-6-nitrotoluene					3.13	8
2,4-Dinitrotoluene	1.52	1	2.25E-13	3		
2,6-Diamino-4-nitrotoluene					2.54	8
2,6-Dinitrotoluene	1.54	1	2.25E-13	3	1.8	3
2-Amino-4,6-Dinitrotoluene					0.36	8
2-Nitrotoluene			7.00E-13	3		
3-Nitrotoluene			9.50E-13	3		
4-Amino-2,6-Dinitrotoluene						
4-Nitrotoluene			7.72E-13	3		
Ammonium Picrate	1.72	1	1.13E-15	3		
HMX (Cyclotetramethylenetrinitramine)			3.30E-10	3		
Nitrobenzene	1.2	1	1.40E-13	3		
Nitrocellulose						
Nitroglycerin	1.6	1				
o-Chlorobenzylidenemalononitrile						
PETN (Pentaerythritol tetranitrate)			1.62E-12	3		
Picric Acid	1.76	1	3.69E-14	3	0.38	3
RDX (Cyclotrimethylenetrinitramine)	1.83	1				
Styphnic Acid			2.81E-13	3		
Tetranitrocarbazole						
Tetryl	1.57	1	1.27E-12	3		

Hughes, J.B., Shanks, J., Vanderford, M., Lauritzen, J., and Bhadra. R. 1996. Transformation of TNT by aquatic plants and plant tissue cultures. Env. Sci. and Tech. 31:266-271.

Hundal, L.S., Shea, P.J., Comfort, S.D., Powers, W.L., Singh, J. 1997. Long-term TNT sorption and bound residue formation in soil. J. Env. Quality. 26: 896-904.

IRP. 1994. Risk Assessment Handbook. Massachusetts Military Reservation. Cape Cod, MA.

IT Corporation. 1997. Investigation of Load Lines at Louisiana Army Ammunition Plant, draft report, July.

Jacobs Engineering Group. 1997a. Massachusetts Military Reservation Inorganics Investigation Technical Memorandum, draft, Document # AFC-J- 23-35K78411-M17-001, prepared for HQ AFCEE/MMR.

Jacobs Engineering Group. 1997b. Draft CS-19 Groundwater Supplemental Site Inspection Report Massachusetts Military Reservation.

Jenkins, T. F. 1997a. Cold Regions Research and Engineering Laboratory. Personal communication with M. Gerath of Ogden Environmental and Energy Services. April 23, 1997.

Jenkins, T. F. 1997b. Cold Regions Research and Engineering Laboratory. Personal communication with M. Gerath of Ogden Environmental and Energy Services. August 11, 1997.

Jenkins, T. F., Grant, C.L., Brar, G.S., Thorne, P.G., Ranney, T.A., and Schumacher, P.W. 1996. Assessment of sampling error associated with collection and analysis of soil samples at explosives-contaminated sites. CRREL. Special Report 96-15. September 1996. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Jerger, D.E., Simon, P.B., Weitzel, R.L., and Schenk, J.E. 1976. Aquatic Field Survey at Iowa Radford and Joliet Army Ammunition Plants. Vol. III: Microbiological Investigation. Ann Arbor, MI: Environmental Control Technology Corporation.

Kaplan, D. 1995. Biotechnology and Bioremediation for Organic Energetic Compounds, U.S. Army Natick Research, Development and Engineering Center, Research Paper # 95-41407-0-3.

Kent, D. 1997. US Geological Survey. Personal communication with M. Gerath of Ogden Environmental and Energy Services. July 31, 1997.

Kitchens, J.F., Harward, W.E.., Lauter, D.M., Wentsel, R.S., and Valentine, R.S. 1978. Preliminary Problem Definition Study of 48 Munitions-Related Chemicals. Prepared for US Army Medical Research and Development Command.

Koch, D. Personal Communication, June 1997, Presentation by D. Harrelsson on May 20, 1997. Preliminary Finding of the U. S. Army Waterways Experiment Station Study of the Natural Attenuation of explosives in Groundwater.

Lagas, P., Loch, J., Bob, C.M., and Gerringa, L. 1984. The bahavior of barium in a landfill and the underlying soil. Water, Air, and Soil Pollution. 22:121-129.

Leckie, J.O., Appleton, A.R., Ball, N.B., Hayes, K.F., and Honeyman, B.D. 1984. Adsorptive removal of trace elements from water with iron oxyhydroxide. Electric Power Research Institute Publication RP-9100-1.

LeBlanc, D.R. 1984. Sewage Plume in Sand and Gravel Aquifer, Cape Cod, Massachusetts. U.S. Geological Survey Water-Supply Paper 2218.

Leggett, D.C. 1985. Sorption of Military Explosive Contaminants on Bentonite Drilling Muds, CRREL Report 85-18, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Li, Z., Comfort, S.D., Shea, P.J. 1997. Destruction of 2,4,6-trinitrotoluene by Fenton oxidation. J. Env. Quality. 26:480-487.

Li, Z., Marx, K.A., Walker, J., and Kaplan, D.L. 1997. Trinitrotoluene and metabolites binding to humic acid. Env. Sci. and Tech. 31:584-589.

Loehr, R.C., 1989. Treatability Potential for EPA Listed Hazardous Wastes in Soil. EPA/600/2-89/001, USEPA-ORD, F.S. Kerr Environmental Research Laboratory, PB89-166581.

Lund, M., J. Davis and Murray, F. 1991. The fate of lead from duck shooting and road runoff in three western Australian wetlands. Australian J. Mar. Fresh. Res. 42:139.

Lyman, W.J., Reehl, W.F., and Rosenblatt, D.H. 1982. Handbook of Chemical Property Estimation Methods. New York: McGraw-Hill.

Manninen, S., and Tanskanen, N.. 1993. Transfer of lead from shotgun pellets to humus and three plant species in a Finnish shooting range. Arch. Environ. Sci. Technol. 29:1219.

MMR. 1997. MMR Installation Restoration Program. Environmental Assessment History- www.mmr.org/mmrl/enviro.htm.

Masterson, J P et al. 1996. Use of particle tracking to improve numerical model calibration and to analyze groundwater flow and contaminant migration, Massachusetts Military Reservation, Western Cape Cod, Massachusetts. US Geological Survey. Open File Report 96-214.

Masterson, J P et al. 1997. Hydrogeologic framework of western Cape Cod, Massachusetts. US Geological Survey. Open File Report 96-465.

Masterson, J.P., and Barlow, P.M. (1994). Effects of simulated ground-water Pumping and recharge on ground-water flow in Cape Cod, Martha's Vineyard and Nantucket Island Basins, Massachusetts. U.S. Geological Survey Open-File Report 94-316.

McCormick, N.G., Cornell, J.H., and Kaplan, A.M. 1984. The fate of RDX and related compounds in anaerobic denitrifying continuous culture systems using simulated wastewater. US Army Natrick Research and Development Laboratory Report Number TR/85/008.

McCormick, N.G., Cornell, J.H., and Kaplan, A.M. 1981. Biodegradation of Hexahydro-1,3,5-trinitro-1,3,5,-triazine. Applied and Environmental Microbiology 42(5), 817-823.

McGrath, C. J. 1995. Review of Formulations for processes Affecting Subsurface Transport of Explosives. Report IRRP-95-2. U. S. Army Corps of Engineers Waterways Experiment Station.

McGrath, C.J. 1996. Updated version of Physical, Chemical, and Environmental Data for Common, Explosive- Associated Compounds (XACs) tables.

McMaster, B.N., Sosebee, J.B., Geden, M.J., and Riley, R.J. 1982. Archive search of the former Eire Army Depot, Ft. Clinton, OH. Prepared for US Army Toxic and Hazardous Materials Agency.

Merck. 1989. The Merck Index. Rahway, NJ.

Morin, K.A., Cherry, J.A., Dave, N.K., Tjoe, P.L., and Vivyurka, A.J. 1988. Migration of acidic groundwater seepage from uranium-tailings impoundments. 1. Field study and conceptual hydrogeological model. J. of Contaminant Hydrology. 2:271-283.

Myers, T.E., Brannon, J.M., Pennington, J.C., Townsend, D.M., Davis, W.M., Ochman, M.K. Hayes, C.A., and Myers, K.F., Laboratory Studies of soil sorption/Transformation Kinetics for Explosives, Technical report in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Ogden. 1997a. Draft Range Use History Report. Prepared for the National Guard Bureau.

Ogden. 1997b. Draft Chemical Composition of Munitions Report. Prepared for the National Guard Bureau.

Palazzo, A.J. and Leggett, D.C. 1986. Effect and disposition of TNT in a terrestrial plant and validation of analytical methods. CRREL Special Report #86-15. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Pennington, J.C. 1997. US Army Corps of Engineers. Waterways Experimental Station. Personal communication with M. Gerath of Ogden Environmental and Energy Services. August 8, 1997.

Pennington, J.C. and Patrick, W.H. 1990. Adsorption and Desorption of 2,4,6-Trinitrotoluene by Soils. Journal of Environmental Quality. 19:559-567.

Pennington, J.C., Hayes, C.A., Myers, K.F., Ochman, M., Gunnison, D., Felt, D.R., and McCormick, E.F. 1995a. Fate of 2,4,6-trinitrotoluene in a Simulated Compost System, Chemosphere. 30: 429-438.

Pennington, J.C., Myers, K.F., Davis, W.M., Olin, T.J., McDonald, T.A., Hayes, C.A. and Townsend, D.M. 1995b. Impacts of Sorption on in situ Bioremediation of Explosives-Contaminated Soils. Technical Report IRRP-95-1, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Phillips, L. 1995. Nonpoint Source Pollution Assessment at Small Arms Firing Ranges. Presentation to Water Environment Federation Annual Meeting. Miami, FL.

Potts, D.B., Shepard, B.K. and Modi, A. 1993. Lake Michigan sediment contamination from 73 years of trap and skeet shooting. Water Science Technology. 28:383.

Price, C.B., Brannon, J.M., and Hayes, C.A. 1997. TNT Transformations: An Exhaustible or Continuing Process, Technical Report in preparation, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Price, C.B., Brannon, J.M., and Hayes, C.A., 1995. Transformation of 2,4,6-trinitrotoluene under controlled Eh/pH Conditions. Technical Report IRRP-95-5, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Qaisi, K.M., Ro, K.S., Reible, D., Thibodeaux, L.J., Valsaraj, K.T., and Constant, W.D. 1996a. Transport process of TNT from flooded highly contaminated surface soil bed. J. Env. Sci. Health. 31:2515-2532.

Qaisi, K.M., Thibodeaux, L.J., and Adrian, D. 1996b. Aquatic plant augmented TNT degradation - analysis of reaction kinetics. J. of Env. Sci. and Health. 31:1595-1603.

Rea, B.A., Kent, D.B., Anderson, L.C.D., Davis, J.D., and LeBlanc, D.R. 1996. The transport of inorganic contaminants in a sewage plume in the Cape Cod Aquifer, Massachusetts. In US Geological Survey Toxic Substance Hydrology Program - Proceedings of a Technical Meeting, Colorado Springs, CO. September 20-24, 1993. USGS Water Resources Investigations Report 94-4015.

Ro, K S, Venugopal, A., Adrian, D, Constant, W D, Qaisi, K M, Valasraj, Ki T., Thibodeaux, L. J., and Roy, D. 1996. Solubility of 2,4,6-Trinitrotoluene (TNT) in Water. Journal of Chemical and Engineering Data. 41:758.

Schmelling, D.C., Gray, K.A., and Kamat, P.V. 1996. Role of reduction in the photocatalytic degradation of TNT. Env. Sci. and Tech. 30:2547-2555.

Schnoor, J.L, Sato, C., McKechnie, D., and Sahoo, D. 1987. Processes, Coefficients, and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters. US EPA Publication EPA/600/3-87-015.

Schwarzenbach, R.P., Gshwend, P.M., and Imboden, D.M. 1993. Environmental Organic Chemistry. New York: John Wiley.

Selim, H.M., and Iskandar, I.K. 1994. Sorption-desorption and Transport of TNT and RDX in Soils. CRREL Report 94-7. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Sikka, H.C., Bannerjee, S., Pack, E.J., and Appleton, H.T. 1980. Environmental Fate of RDX and TNT. US Army Medical Research and Development Command, Fort Detrick, MD.

Spain, J.C. 1995. Biodegradation of Nitroaromatic Compounds. New York: Plenum Press.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press.

Syracuse Research Corp. 1993. Toxicological Profile for Chromium. Prepared for the Agency for Toxic Substances and Disease Registry.

Thorne, P.G. and Leggett, D.C. 1997. Hydrolytic release of bound residues from composted soil contaminated with 2,4,6-trinitrotoluene. Env. Tox. and Chem. 6:1132-1134.

Thurman, E.M., Barber, L.B., and LeBlanc, D.R. 1986. Movement and fate of detergents in groundwater. A field study. J. of Contaminant Hydrology. 1:143-161.

Townsend, D.M. Adrian, D.D., and Meyers, T.E. 1996. RDX and HMX Sorption in Thin Disk Soil Columns. Technical Report IRRP-96-, U.S. Army Corps of Engineers Waterways Experiment Station.

Townsend, D.M. and Meyers, T.E. 1996. Recent Developments in Formulating Model Descriptors for Subsurface Transformation and Sorption of TNT, RDX, and HMX. Technical Report IRRP-96- 1, U.S. Army Corps of Engineers Waterways Experiment Station.

US Army. 1984. Military Explosives. TM9-1300-214.

U.S. Army Center for Health Promotion and Prevention Medicine (USACHPPM). 1996. Draft Final Site Inspection Report, Geophysical Study No. 38-26-K33U-95, Sites CS-18 and CS-19, Massachusetts Military Reservation, Cape Cod, Massachusetts. June.

U.S. Army Center for Health Promotion and Prevention Medicine (USACHPPM). 1996. Draft Final Site Inspection Report, No. 38-26-1339-95, Site CS-19, Massachusetts Military Reservation, Cape Cod, Massachusetts. June.

U.S. Army Corp. of Engineers Waterways Experiment Station (WES). 1996. Draft Report Vertical Migration Potential of Metal Contaminants for Small Arms Firing Ranges at Camp Edwards Military Reservation.

U.S. Environmental Hygiene Agency (USAEHA). 1987. Interim Report, Hazardous Waste Study No. 37-26-0165-87, Investigation of Soil Contamination from Propellant Burns, Camp Edwards, Massachusetts, 25-29 June and 14-15 July, 1987. September.

Walsh, M.E. 1990. Environmental transformation products of nitroaromatics and nitramines. Literature Review and Recommendations for Analytical Method Development. CRREL Special Report #90-2. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Walsh, M.E. and Jenkins, T.F. 1992. Identification of TNT transformation products in soils. CRREL Special Report #92-16. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

Walsh. M.E., Collins, C.M., and Racine, C.H. 1996. Persistence of White Phosphorus Particles in Salt Marsh Sediments. Environmental Toxicology and Chemistry. 15:846-855.

Walter, D. 1997. US Geological Survey. Personal communication with M. Gerath of Ogden Environmental and Energy Services. July 30, 1997.

Weissmahr, K.W., Haderlein, S.B. and Schwarzenbach. R.P. 1996. In situ spectroscopic investigations of adsorption mechanisms of nitroaromatic compounds at clay minerals. Env. Sci. and Tech. 31:240-247.

Xu, H., Allard, B., and Grimvall, A. 1991. Effects of acidification and natural organic materials on the mobility of arsenic in the environment. Water, Air, and Soil Pollution. 57:269-278.

Xue, S. K. 1995. Adsorption-Desorption of 2,4,6-Trinitrotoluene and Hexahydro-1,3,5-Trinito-1,3,5-Triazine in Soils. Soil Science 160:317-327.

Xue, S. K. 1995. Transport of 2,4,6-Trinitrotoluene and Hexahydro-1,3,5-Trinitro-1,3,5-Triazine in soils. Soil Science. 160:325-339.

JONATHAN BOURNE PUBLIC LIBRARY
0 0113 0087050 5

For Reference
Not to be taken from this room

Jonathan Bourne Public Library
19 Sandwich Rd.
Bourne, MA 02532